

CATANIONIC SURFACTANTS

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PÄIVI JOKELA



LUND 1986



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PÄIVI JOKELA

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CATANIONIC SURFACTANTS

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Abstract The phase equilibria of aqueous systems which contained both a cationic and an anionic amphiphile (catanionic systems) were studied. Experimental phase diagrams were determined for binary catanionic surfactant - water systems. Moreover, phase equilibria were studied in ternary systems where a charged or an uncharged amphiphile, respectively, were added to the binary systems. The experimental techniques used were ^2H NMR, X-ray diffraction and polarizing microscopy. A lamellar phase in equilibrium with the catanionic crystals on one side and with an aqueous phase on the other side was observed in these systems. When the temperature was increased the lamellar phase became more stable relative to the crystals, but above the melting point of the crystals a reversed micellar phase gradually replaced the lamellar phase. Thermodynamic model calculations were used for determining the phase boundaries between a lamellar phase and crystalline phases, and also between two lamellar phases with different water contents. The calculations showed that small amounts of an ionic surfactant in the systems made the electrostatic repulsion comparable with the attractive interaction from the van der Waals force. The hydration force interaction between the uncharged lamellar bilayers was also studied in these systems. In the binary systems the hydration force became stronger with increasing size of the polar head group of the catanionic surfactant. After an addition of a charged amphiphile the swelling of the lamellar phase increased drastically, but an addition of an uncharged amphiphile also made the swelling increase slightly. These results are discussed in light of the main theories for the hydration force.			
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När allting går lätt,
blir man fort dum.

Maxim Gorkij

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LIST OF PAPERS

The present thesis consists of a summary and the following papers which will be referred to in the text by their Roman numerals.

I Phase equilibria in the sodium octanoate - octylammonium octanoate - water system

P. Jokela, B. Jönsson, B. Eichmüller and K. Fontell, *Langmuir*, submitted for publication.

II Phase equilibria of catanionic surfactant - water systems

P. Jokela, B. Jönsson and A. Khan, *J. Physical Chemistry*, submitted for publication.

III Phase equilibria of catanionic surfactant - dodecanol - water systems

P. Jokela and B. Jönsson, to be published.

IV Phase equilibria in systems containing both an anionic and a cationic amphiphile. A thermodynamic model calculation.

P. Jokela, B. Jönsson and H. Wennerström, *Progr. Colloid & Polymer Sci.*, 70:17 (1985).

INTRODUCTION

This thesis deals with catanionic surfactants which are composed of a cationic and an anionic compound in equimolar ratio. The phase equilibria in aqueous catanionic systems have been studied, and the hydration force interaction between the lamellar bilayers has been of special interest. The phase diagrams for binary systems containing different catanionic surfactants and water (I, II) have been determined experimentally. Furthermore, the phase equilibria have been studied in ternary systems where a charged (I) and an uncharged (II) amphiphile, respectively, are added to the binary systems.

Thermodynamic model calculations have been used for determining the phase boundaries between the lamellar phase and surfactant crystals (IV), and between two lamellar phases with different water contents (I).

The swelling of the lamellar phase in the catanionic systems is discussed in light of the main theories which have been suggested in order to describe the molecular origin of the hydration force. (I, II, III).

The following abbreviations are used: AD denotes dodecylammonium dodecanoate, AS dodecylammonium dodecylsulphate, TAS dodecyltrimethylammonium dodecylsulphate and EDAS dodecylethyldimethylammonium dodecylsulphate.

Amphiphilic systems

The extraordinary physico-chemical properties of aqueous surfactant systems are based on the amphiphilic structure of the surfactants. A surfactant molecule consists of a hydrophilic part which has an affinity to water, and of a hydrophobic part which tends to avoid contact with water. Due to this dualistic structure, the surfactant molecules are readily adsorbed at the interfaces between aqueous solutions and other, less polar, phases. Another important consequence of the amphiphilic structure is the self-association of the surfactant molecules into various types of large aggregates, e.g. micelles and liquid crystalline phases (1 - 3).

Surfactants can be classified on the basis of their polar headgroup, which may be cationic, anionic, nonionic or zwitterionic. In this work, a new term is introduced in addition to the conventional classification: an amphiphilic compound which contains both a cationic and an anionic surfactant in equimolar ratio is referred to as a **catanionic surfactant**. An example of each group of the surfactants is shown in Fig. 1.

Even in binary surfactant - water systems a large number of phases may occur, and when a third component is added to the binary systems the phase behaviour usually becomes even more complicated (4 - 20). As an example of the rich variety of different phase structures, a triangle diagram of the ternary system sodium octanoate - decanol - water (5, 19, 20) is shown in Fig. 2. The symbols used to denote different phase structures are based on Ekwall's system (8, 13).

The L_1 and L_2 phases are homogeneous isotropic solutions. The L_1 phase



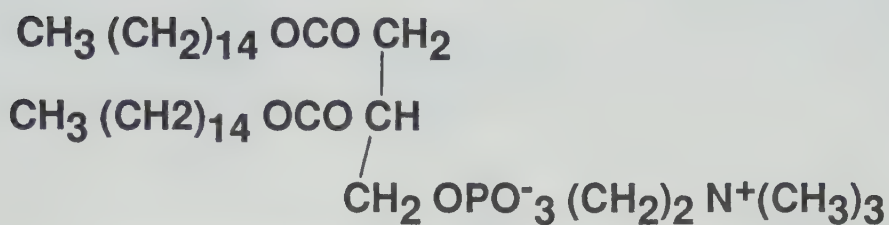
a) hexadecyltrimethylammonium
bromide (CTAB)



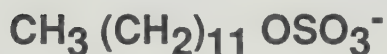
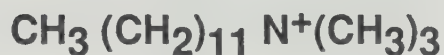
b) octadecanoic acid



c) pentaoxyethylene dodecylether



d) dipalmitoyllecithin



e) dodecyltrimethylammonium
dodecylsulphate (TAS)

Fig. 1 Chemical formulae of a) a cationic, b) an anionic, c) a nonionic, d) a zwitterionic and e) a **catanionic** surfactant.

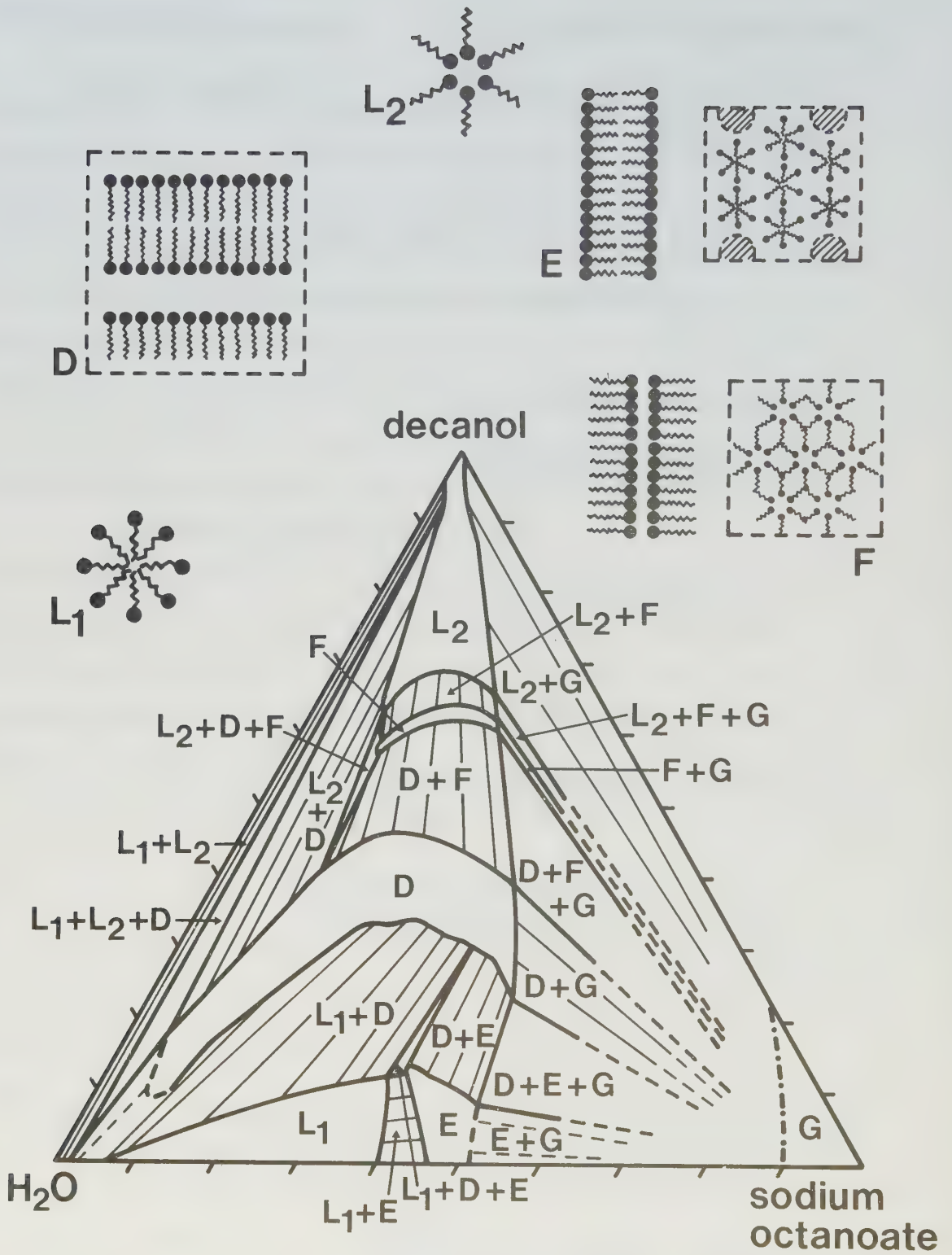


Fig. 2 Phase diagram of the ternary sodium octanoate - decanol - water system redrawn after ref. (5), (19) and (20). Schematic structures of different phases are inserted.

contains micellar aggregates in aqueous solution. The size and the shape of the aggregates depend on the nature and the concentration of the surfactant, but they have in common that the hydrocarbon chains lie in the interior of the aggregates surrounded by the polar groups. In the same way, the L_2 phase consists of reversed micellar aggregates in an alcohol solution. In a reversed micelle, water and the polar headgroups form the core of the aggregates while the hydrocarbon chains are in contact with the bulk solution.

One of the most important properties of the micellar solutions is their capability of solubilizing substances that otherwise would be insoluble in the bulk solution (2, 11, 21). For example, strongly hydrophobic substances can be incorporated in the hydrophobic interior of normal micelles, while weakly polar substances may form mixed micelles with the solubilizing agent. Analogously, reversed micelles may be able to incorporate some hydrophilic molecules in the polar interior of the aggregates.

Increasing surfactant concentration and addition of a third component to the surfactant - water systems may lead to a formation of liquid crystalline mesophases (for an overview, see ref. 3 and 21). Liquid crystalline phase structures can be considered as intermediate states between crystalline solids and liquids. On one hand, they have a long-range crystalline order which, for example, makes it possible to study them by X-ray diffraction techniques (22). But on the other hand, the molecular motion in a liquid crystalline structure is rapid, as in a liquid.

There are three well-established classes of liquid crystalline phases: lamellar (D), hexagonal (E and F) and cubic (I). The lamellar mesophase consists of surfactant bilayers alternating with water layers, while the hexagonal phases are composed of long cylindrical aggregates which are packed in a hexagonal array. In a normal hexagonal phase (E), the hydrocarbon chains form the core of each cylinder and the polar groups lie on the surface. In a reversed hexagonal phase (F), the hydrophobic groups occupy the spaces between the hexagonally packed water cylinders.

Both the lamellar phase and the hexagonal phase are optically anisotropic, and they can be identified by the typical textures they show in a polarizing microscope (4). Contrary to this, the cubic phase is optically isotropic. The structure of the cubic phase is not as well-established as that of the other liquid crystalline phases. As the cubic phase can appear at very different positions relative to the other phases, it is assumed that the phase structure is also different depending on where in the phase diagram this phase is located (3, 17, 21). An example of a suggested structure for a cubic phase (23) is shown in Fig. 3. This structure is built from lamellar aggregate units, and it can be shown (24, 25) that the plane of the methyl end groups in the bilayers form an infinite periodic minimal surface.

Catanionic systems

The phase equilibria of various anionic and cationic amphiphilic systems have been studied in great detail, both experimentally (13) and theoretically (26 - 28), but there are only a few studies of catanionic

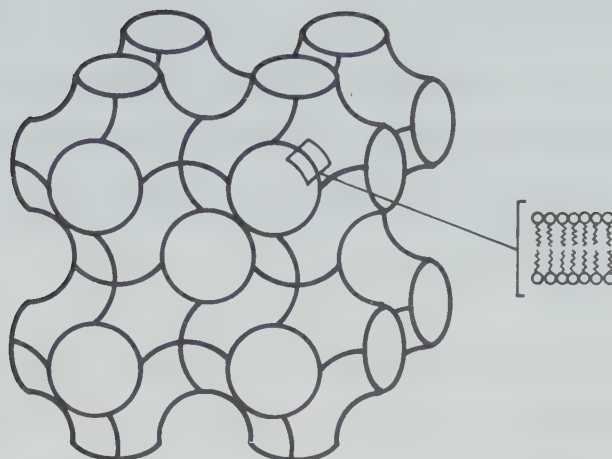


Fig. 3 Proposed structure of a cubic phase built from lamellar aggregate units (24).

surfactant systems (29 - 36, I - IV). The catanionic systems can, however, show very interesting phase behaviour which may be quite different from the systems where only the cationic or the anionic surfactant is present.

The aim of the present work has been to investigate the properties of the catanionic systems in a more systematic way, and the repulsive hydration force interaction in the systems has been of special interest (37 - 68).

Articles I, II and III are experimental studies of the phase equilibria in different catanionic systems. The ternary phase diagram for a catanionic surfactant - anionic surfactant - water system is determined in article I.

In article II, binary catanionic surfactant - water systems are studied, and in article III an uncharged amphiphilic molecule is added to the binary system. Finally, article IV is a theoretical model calculation of phase equilibria in a four-component system which contains a catanionic, a cationic and an anionic surfactant in water.

When the hydration force interaction in the catanionic systems is studied experimentally, it is of great importance that the surface charge density of the surfactant aggregates can be neglected. Therefore, the studied catanionic systems are chosen so that they fulfill the following conditions:

- 1) The catanionic surfactants are composed of a cationic and an anionic surfactant in equimolar ratio.
- 2) The concentration of the inorganic counterions is negligible.

In article II, it is shown that the surface charge density in a lamellar system is a function of both the hydrocarbon chain length of the surfactants and the thickness of the water layer between the lamellar aggregates. Consequently, an additional condition is obtained:

- 3) The cationic and the anionic surfactants have the same hydrocarbon chain length, or the hydrocarbon chains contain at least eight carbon atoms. Therefore, the two ionic surfactants have approximately the same solubility in water.

METHODS

The experimental techniques used to determine the phase diagrams were deuterium NMR, X-ray diffraction and polarizing microscopy.

a) ^2H NMR

^2H NMR method has been used successfully for experimental studies of the phase equilibria in various amphiphilic systems (69 - 79). This method is especially convenient for determining the phase boundaries between an anisotropic phase and a two-phase region with an anisotropic and an isotropic phase because it can detect very low concentrations of an isotropic phase. Furthermore, when the water in the studied system is displaced by heavy water, the deuteron quadrupole splittings can give information on water which is incorporated in the liquid crystals.

The theoretical background of the NMR-technique is described in detail in several references (80 - 83), and a brief summary of the theory is given in article II. When a nucleus with a spin quantum number >1 is placed in an external magnetic field, the interaction between the quadrupole moment of the nucleus and an electric field gradient in the nuclear environment may give rise to a deuteron quadrupole splitting. In an isotropic solution, however, the interaction is averaged to zero by the rapid molecular motion, and only a single sharp peak is observed. In an anisotropic liquid crystalline phase, the frequency signal may split into two equally intense peaks. If several phases are present, the NMR spectrum is a superposition of the different spectra. For example, if the sample contains two different anisotropic phases and an isotropic phase, two doublets and a central singlet will be observed.

b) X-ray diffraction

The structure of the liquid crystalline phases may be identified by X-ray diffraction technique (22). A typical diffraction pattern for amphiphilic liquid crystals consists of a broad diffuse reflection at the wide angle region, but in the low angle region, i.e. at the angular range near the primary beam, the relative positions of the reflections depend on the liquid crystalline phase structure. For the lamellar phase, the X-ray diffraction thus gives sharp Bragg reflections in the ratio $1 : 1/2 : 1/3 : 1/4$, whereas the reflections in the hexagonal phase structures have the ratio $1 : 1/\sqrt{3} : 1/\sqrt{4} : 1/\sqrt{7}$. The cubic phase can also be identified by this method, but the different cubic phase structures show different reflection patterns.

In addition, the crystalline phases can easily be detected by the diffraction technique, as the crystalline phase structure shows a series of sharp reflections at the wide angle region, too.

c) Polarizing microscopy

Polarizing microscopy (4) provides a supplementary method of identifying different phase structures, since both anisotropic liquid crystalline phases exhibit distinct textures when studied between crossed polaroids. The lamellar phase structure is best identified by the mosaic pattern while the hexagonal phases usually show a non-geometric texture. The existence of crystals is also easily confirmed by this method.

The definitive identification of the phase structures is then made by

combining the information obtained from different experimental methods, and also by considering the location of the different phase structures relative to each other in the phase diagram.

In some cases, the phase boundaries can also be determined by making use of the experimental data in an alternative way. When the two-site model was applied to the lamellar phase in article II, the deuteron splittings could be used for determining the phase boundary between the lamellar phase and the two-phase region which contains the lamellar phase and an isotropic solution.

In article III, two-phase samples which contain two isotropic phases (L_2 and water) were used to estimate the phase boundary of the L_2 phase.

THE EXPERIMENTAL PHASE DIAGRAMS

In order to investigate how the addition of a catanionic surfactant affects the stability of the different phase structures, the phase behaviour of the catanionic systems has been compared with previously determined phase equilibria of ionic systems. In article I, the alcohol is replaced by a catanionic surfactant in the ternary system of sodium octanoate - decanol - water (c.f. Fig. 2), and the phase diagram for the sodium octanoate - octylammonium octanoate - water system is determined at 298 K. Up to the octylammonium octanoate concentration of 50 % w/w, the catanionic phase diagram is very similar to the well-established phase diagram in Fig. 2. However, above this concentration, the catanionic system does not

form reversed micellar or reversed hexagonal phases, but instead the lamellar phase is in equilibrium with both crystalline phases in the system.

Another important feature is that the lamellar phase of the catanionic system is also stable in a small region along the binary octylammonium octanoate - water axis.

The phase equilibria of the binary octylammonium octanoate - water system as a function of temperature is also studied in article I, and some other binary catanionic surfactant - water systems are investigated in article II. The studied catanionic compounds AD, AS, TAS and EDAS have the same hydrocarbon chain length but different polar head groups. The experimental phase diagrams of the binary systems confirm that above the Krafft temperature and below the eutectic melting point of the surfactant, only one liquid crystalline phase, the lamellar phase, is present. The lamellar phase is in equilibrium with almost pure water on one side, and with the surfactant crystals on the other side.

It is interesting to study how the phase behaviour changes when an uncharged amphiphile is added to a binary catanionic surfactant - water system. In article III, phase diagrams for two different catanionic surfactant - dodecanol - water systems are determined at 333 K. The catanionic surfactants used are AD and TAS.

At low dodecanol concentrations the phase equilibria in both systems resemble the binary catanionic surfactant - water system, showing a lamellar phase in equilibrium with a water phase and surfactant crystals. Further addition of dodecanol to the systems favours the formation of a reversed hexagonal phase, and at still higher alcohol concentrations a

reversed micellar phase appears.

Some important differences between the two phase diagrams were also observed. The extension of the lamellar phase in the AD system was strongly reduced compared to the TAS system. Furthermore, it was observed in the AD system only that the reversed micellar phase was extended to very high concentrations of the catanionic surfactant. This phase was assumed to have melted surfactant instead of dodecanol as the continuous phase.

Temperature dependent effects

An interesting peculiarity of the catanionic systems was that the appearance of the ternary phase diagrams may change quite drastically with increasing temperature (I - III). This is mainly due to the relatively strong temperature dependence of the phase equilibria between the lamellar phase and the surfactant crystals. The binary phase diagrams of the catanionic surfactant - water systems (I, II) show that below the eutectic melting point of the surfactant crystals, increasing temperature favours the extension of the lamellar phase. But when the surfactant crystals begin to melt, an isotropic phase appears at the waterpoor part of the phase diagram, and this isotropic phase becomes more stable relative to the lamellar phase with increasing temperature. The lamellar phase disappears totally at relatively low temperatures (348 - 383 K, depending on the catanionic surfactant). It is interesting to notice that the melted catanionic surfactant is able to form reversed micellar aggregates which can incorporate some water, and in ternary systems, also other amphiphilic molecules (I, III).

In the octylammonium octanoate - sodium octanoate - water system (I), a reversed micellar phase, L_2 , begins to form already at 310 K in the octylammonium octanoate corner of the diagram, and it extends towards higher water contents with increasing temperature, while the extension of the lamellar phase becomes more and more suppressed.

In the same way, the differences in the phase behaviour of the two ternary catanionic surfactant - dodecanol - water systems (III) are a result of the temperature-dependent balance between the lamellar phase and the surfactant crystals. The phase diagrams are determined at 333 K, and this temperature is below the eutectic melting point of the TAS crystals, but above that of the AD crystals. This is one of the reasons why the stability of the lamellar phase in the AD system is so strongly reduced compared to the lamellar phase of the TAS system; and that is why this trend becomes even more striking with increasing temperature. The other contribution to this difference in the phase equilibria is a weaker hydration force repulsion in the AD system, which is discussed in the next section.

HYDRATION FORCE

The double-chained cationic surfactants have a chemical composition similar to zwitterionic phospholipids, such as lecithin or phosphatidyl-ethanolamine (see Fig. 1), and our experimental studies showed that the phase behaviour of binary cationic surfactant - water systems also is parallel to that of a lecithin - water system (6, 84 - 90). Above the Krafft temperature, only one liquid crystalline phase, the lamellar phase, is present. The solubility of the cationic molecules in water is assumed to be very low, so that the lamellar phase is in equilibrium with almost pure water through a large two-phase region (I, II).

As the lamellar aggregates are uncharged, it was assumed that the dominating forces between the lamellar bilayers are the attractive van der Waals force and the repulsive hydration force (37 - 68).

A brief overview of the hydration force is given in article II. The force is a strong, exponentially decaying repulsive force with a decay length of 0.2 - 0.3 nm for lipid bilayers and 1.0 nm for hard surfaces, such as mica, and it can be described by the empirical equation

$$P_{HF} = P_0 * \exp (-d/\lambda) \quad (1)$$

where P and d are the pressure and the distance between the surfaces, and λ and P_0 are constants that are specific for each system. The hydration force can be considered as a special case of the solvation forces, since it has only been observed between two hydrophilic surfaces in an aqueous medium.

The theoretical understanding of this interaction is still limited, although several theories have been suggested in order to describe its molecular origin (60 - 68). One of the main theories has been suggested by Marcelja, Gruen and coworkers (61 - 66); they have considered an aqueous layer between two parallel, planar surfaces. A polarization field induces an orientation of water molecules in the vicinity of the surfaces. This results at short range in an exponentially decaying force between the surfaces.

Jönsson and Wennerström have suggested a theoretical model for phospholipid bilayer systems (67, 68). According to this theory, both water and the hydrocarbon layers are treated as continuous media, and the interaction between the bilayers is due to the dielectric discontinuities at the water-hydrocarbon interfaces. The dependence of the osmotic pressure between the bilayers as a function of the distance between them can be calculated, but in this case the theoretical equation becomes more complicated than the empirical one, eq. (1).

Aqueous zwitterionic phospholipid systems are often employed in studies of the hydration force interaction between lamellar bilayers. In a series of papers, Parsegian and coworkers have studied these systems experimentally (38 - 45), and phospholipid bilayers are also used as model systems in theoretical calculations (60, 67, 68). However, the interface between the lecithin bilayer and water seems to be rather difficult to describe in theoretical models, because the choline groups of the zwitterionic lecithin molecules are not fixed in well-defined positions relative to the interface. The advantage of studying the bilayers which are formed by catanionic molecules is that we can assume that both the positive and negative head groups are lying at the same distance from the

hydrocarbon surface (I, II). Consequently, catanionic surfactant - water systems should be more suitable for theoretical model studies of the hydration force.

In article II, the size of the polar headgroup of the studied catanionic surfactants is systematically increased, in order to investigate the effect of the headgroup on the repulsive hydration force between the lamellar bilayers. The experimental results show that in the studied systems the strength of the hydration force is more dependent on the size of polar headgroups than on their specific chemical composition. When the polar head group becomes larger, the maximum uptake of water in the lamellar phase increases. In contrast to the relatively strong temperature dependence of the balance between the lamellar phase and the surfactant crystals, the swelling of the lamellar phase increases only slightly with increasing temperature. This trend can, however, easily be observed from the deuterium NMR spectra (II).

The experimental results are also discussed in the light of the two main theories which are suggested for the hydration force (61 - 68). In the studied systems, the interactions between the lamellae are better described by the theory that treats water as a continuous media than by the model which is based on the surface-induced changes in the water structure.

The catanionic systems are apparently not able to swell as much as the zwitterionic phospholipid systems (45, 84, 89, 90). This fact is first discussed in article I, where the empirical equation (1) is used to describe the hydration force interaction between the lamellar bilayers. According to this model, there may be two contributions to the weaker

hydration force repulsion in the catanionic systems compared with the zwitterionic ones: either the force is weaker for all distances or the decay length of the force is smaller. In article II, it is shown that the continuum theory is able to predict the weaker hydration force repulsion in the catanionic systems, but it is also pointed out that the comparison of these two kinds of systems is not straightforward.

In the binary catanionic surfactant - water systems (I, II), the dominating interactions between the uncharged lamellar bilayers were assumed to be the attractive van der Waals force and the repulsive hydration force. As the hydration force repulsion has a relatively short range, the maximum uptake of water in the lamellar phase of these systems was in the range 19 - 35 % w/w.

In article I, a charged amphiphile was added to a binary catanionic surfactant - water system, which gave rise to an electrostatic repulsion between the bilayers. The electrostatic repulsion operates at longer distances than the hydration force; therefore, the charged lamellar aggregates are able to swell much more than the uncharged ones. In addition, the attractive dispersion force in hydrocarbon - water systems is relatively weak compared with the electrostatic forces in ionic lamellar systems, and very small amounts of the ionic amphiphile can thus produce an electrostatic repulsion that is comparable with the attractive interaction.

The experimental phase diagram in article I showed that an addition of 3% w/w sodium octanoate to the binary octylammonium octanoate - water system made the lamellar phase swell from a water content of 25 % w/w to 80 % w/w. Theoretical calculations of the phase equilibria in the same

system predicted that the electrostatic double layer repulsion begins to dominate over the van der Waals interaction if the lamellar aggregate contains only 1 % w/w of a charged amphiphile.

In article III, an uncharged amphiphile is added to binary cationic surfactant - water systems. The experimental phase diagrams show that the maximum uptake of water in the lamellar phase increases when dodecanol is added to the binary systems of AD - water and TAS - water, respectively. This increase in swelling is, however, quite modest compared to the effect of the added charged component.

In this case, it may be more difficult to find an explanation for the change in the swelling of the lamellae. An addition of an uncharged amphiphile will not lead to any electrostatic repulsion, but the dominating forces between the bilayers are still the van der Waals attraction and the hydration force repulsion.

The continuum theory (67, 68) may, however, be also applied to this system. According to this theory, there are two contributions to the hydration force interactions: a repulsive image charge and an attractive correlation interaction. The maximum uptake of water in the lamellar system can then be calculated using the condition that the attractive and the repulsive contributions of the hydration force balance each other at that bilayer separation. The calculated phase boundary shows that when the charge concentration in the lamellar aggregates is diluted by the addition of the uncharged amphiphile, the attractive contribution decreases more rapidly than the repulsive one. This leads to an increasing repulsive net force between the bilayers.

THERMODYNAMIC MODEL

In articles I and IV, a thermodynamic model is used for calculations of the phase equilibria in the catanionic systems. The ternary system in article I contains a catanionic and an anionic surfactant in water. The studied system in article IV consists of four component: a catanionic (A^+A^-), a cationic (A^+X^-), and an anionic (A^-X^+) surfactant, and water. Furthermore, the inorganic counterions (X^+ and X^-) are not eliminated from the system. The thermodynamic model has been developed for ionic surfactant systems, and it has previously been presented in a series of papers (26 - 28). However, it is necessary to modify the model slightly when it is applied to the catanionic system. The following assumptions are made in order to describe the model systems:

- 1) The solubility of the surfactant in water is assumed to be so low that all the surfactant molecules are incorporated into the lamellar aggregates. The concentration of the surfactant ions in water should be taken into account only at very high water contents.
- 2) The inorganic counterions are dissolved in the water phase and they are distributed according to the Poisson-Boltzmann theory.
- 3) The aggregate geometries can be of five different types: normal and reversed micelles are assumed to be spherical, the hexagonal phases consist of infinite cylinders packed in a hexagonal lattice, and the lamellar phase of infinite planar sheets. In the studied catanionic systems only the lamellar phase has been considered.

4) In the four-component system, the simple salt formed by the counterions, X^+X^- , is assumed to have so high solubility in water that it is sufficient to consider only the upper part of the trigonal bipyramid.

5) In article I, the catanionic surfactant is able to form an isotropic phase above the eutectic melting point of the surfactant, while in article IV, the A^+A^- crystal is assumed to be particularly stable.

The free energy of the model system may then be written:

$$G = \sum_i n_i \cdot \mu_{i0} + G_s + G_{el} - TS_{mix} + G_{disp} + G_{hf} \quad (2)$$

where μ_{i0} is the standard chemical potential of component i , G_s a surface free energy, G_{el} an electrostatic free energy, T the temperature, S_{mix} the entropy of mixing the components, G_{disp} the free energy from the dispersion interactions and finally G_{hf} a free energy responsible for the hydration force. The last term is not included in the model calculation of the four-component system (IV). The contributions to the chemical potentials from the different free energy terms are described in articles I and article IV.

The surface free energy is assumed to be proportional to the contact area between the aqueous region and the aggregates. The proportionality constant, γ , can be determined experimentally (26, 28).

The contributions from the electrostatic free energy and the entropy of mixing depend on the form and the composition of the aggregate. The free

electrostatic energy also involves a solution of the Poisson-Boltzmann (PB) equation which may become quite complicated. However, for a lamellar system with only counterions in the aqueous region, the PB equation has a simple analytical solution (26, 28).

In contrast to the ionic surfactant systems, the attractive van der Waals force cannot be neglected in the catanionic systems where the surface charge density of the surfactant aggregates is low. The dispersion force energy for an infinite array of water and hydrocarbon sheets is written as an infinite sum, and it is assumed to be zero when $L \rightarrow \infty$ (91).

The energy contribution due to the hydration force is assumed to decay exponentially according to the empirical equation (1) . This approximation is able to describe the repulsive hydration force interaction in article I, where the studied system also contains a charged amphiphile. As was mentioned above, a more detailed theoretical approach is required in order to explain the phase behaviour of the catanionic systems when an uncharged amphiphile is present (III).

By combining these different contributions, the chemical potentials for all the components in the lamellar system may then be calculated. In the catanionic systems, where the charge densities are low, the maximum length of the amphiphilic molecules, $b_{\max}$, is assumed in the calculations. The phase equilibrium between two phases is defined by the condition that the chemical potentials for all components in both phases should be equal.

In article I, the phase equilibria in the lamellar phase between two different water contents are determined. For this purpose, the chemical potential of the catanionic surfactant, μ_{A+A^-} , is chosen to be a constant.

The chemical potentials of the ionic surfactant, $\mu_{A^+X^-}$, and water, μ_{H_2O} , can then be calculated for different values of the water layer thickness, $2L$. When the chemical potentials are plotted in a diagram, $\mu_{A^+X^-}$ as a function of μ_{H_2O} , the resulting curve consists of two parts. The two lamellar phases are in equilibrium in the intersection of these parts, and the corresponding compositions of the phases can be calculated. The process is repeated for different $\mu_{A^+A^-}$ values until a complete phase diagram can be constructed.

The theoretical calculations predict that the attractive van der Waals force between the bilayers gives rise to a mixing gap in the lamellar phase of the binary octylammonium octanoate - water system. However, when only a small amount (1 % w/w) of an ionic surfactant is added to the lamellar system, the electrostatic repulsion will be comparable to the attractive interaction. This leads to a significant increase in the swelling of the lamellar phase.

In the four-component system (IV), the phase boundaries between the lamellar phase and the crystalline phases A^+A^- , A^-X^+ and A^+X^- are calculated. The crystalline salts are assumed to possess constant chemical potentials. Furthermore, there is a complete symmetry with respect to charge inversion in the model, and only one half of the bipyramid is considered.

The calculations are performed by first choosing a plane in the bipyramid and a constant value for the water chemical potential, μ_{H_2O} . The chemical

potentials of the catanionic and one of the ionic surfactants can then be calculated for different values of the water layer thickness, $2L$, and they are plotted in a diagram, $\mu_{A^+A^-}$ as a function of $\mu_{A^-X^+}$. The constant chemical potentials of the crystalline salts represent straight lines in the same diagram, and the lamellar phase is in equilibrium with the crystalline phases at the intersections in the plot. The full phase diagram is obtained after repeating the calculations for new values of μ_{H_2O} , and when the phase boundaries in one plane are determined, a new plane is chosen.

The calculated phase equilibria between the lamellar phase and the crystalline phases show an instability gap between the two lamellar regions around the midplane of the bipyramid, where the lamellar bilayers are assumed to be uncharged. The van der Waals attraction dominates over the electrostatic repulsion in this region and, moreover, the repulsive hydration force is not included in this model calculation. On the other hand, the A^+A^- crystals are assumed to have a constant, relatively low chemical potential compared to the lamellar phase. Consequently, the crystalline phase becomes more stable relative to the lamellar phase in the vicinity of the midplane.

This calculated extension of the lamellar phase relative to the catanionic surfactant crystals is compared with the experimental phase diagrams in article III.

Another interesting feature in the calculated phase equilibria in article IV is that the stability of the lamellar phase relative to the anionic surfactant crystals (A^-X^+) increases when cationic surfactant (A^+X^-) is

added to the binary A^-X^+ - water system. In this case, the lamellar phase is assumed to have a higher entropy than the ionic crystals. The lamellar phase may thus extend to very low water contents near the instability gap between the two lamellar regions.

CONCLUDING REMARKS

This thesis can be viewed as an introduction to more systematical studies of the catanionic surfactants. In order to obtain a deeper understanding of surfactant properties, the phase equilibria of various catanionic systems have been studied experimentally. The characteristic feature of the phase diagrams is the presence of a lamellar phase which is in equilibrium with the catanionic surfactant crystals on one side and with almost pure water phase on the other side.

The lamellar phase first becomes more stable relative to the surfactant crystals when the temperature is increased. But above the melting point of the crystals, a reversed micellar phase appears, and the lamellar phase is gradually replaced by this isotropic L_2 phase.

Furthermore, thermodynamic model calculations were used for determining the phase equilibria. The model was originally developed for ionic surfactant systems, but after minor modifications it can also be applied to the catanionic systems.

As the charge density of the catanionic systems is low, the attractive van der Waals force cannot be neglected in the model calculations. On the

other hand, when only small amounts of an ionic surfactant are added to the system, the electrostatic repulsion becomes comparable with the attractive interaction.

The molecular origin of the hydration force interaction is still under debate; therefore, it was interesting to notice that the electrostatic continuum model obtained support from the experimental studies of the catanionic systems. The model was able to explain the swelling behaviour in the binary surfactant - water systems. Moreover, it was successfully applied to the systems where an uncharged amphiphilic molecule was added to the binary systems.

Much still remains to be done in order to establish the phase equilibria of different catanionic systems. A better understanding of the phase behaviour in these systems may also enrich insight into the hydration force interaction between lamellar bilayers.

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Phase equilibria in the sodium octanoate - octylammonium octanoate - water system

by

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ABSTRACT

The complete phase diagram of the ternary system sodium octanoate - octylammonium octanoate - water has been determined at 298 K. The experimental techniques used were polarizing microscopy and X-ray diffraction. The stability of the lamellar mesophase has also been studied at higher temperatures, above the melting point of octylammonium octanoate which was measured to be between 314 and 315 K, in order to follow the formation of an isotropic solution that partly suppresses the lamellar phase at these temperatures. The experimental observations are discussed in the light of recent theoretical work on double layer and hydration forces in lamellar liquid crystalline systems.

The dominant feature of the phase diagram at 298 K is the large lamellar phase. The lamellar phase is for some water concentrations also stable for the two-component system octylammonium octanoate - water. This stability can only be explained if there is an hydration force operating between the bilayers, in the same way as for the lecithin - water system. The resemblance between the lamellar phase in a lecithin - water system and that in an octylammonium octanoate - water system is rather pronounced, the main difference seems to be that the hydration force is more long ranged in the lecithin-water system.

The extension of the lamellar phase may be increased from 25% w/w to more than 80% w/w of water by adding only small amounts of sodium octanoate. The resemblance between the lamellar phases of octylammonium octanoate and lecithin, respectively, is striking also in this respect.

Introduction

There were two reasons for us to study the ternary system sodium octanoate - octylammonium octanoate - water.

The main reason was that the chemical composition of the octylammonium octanoate reminds of the composition of a zwitterionic phospholipid, such as lecithin or phosphatidylethanolamine. Therefore, it was interesting to study if the binary octylammonium octanoate - water system would show a parallel phase behaviour to a lecithin - water system (1, 2). The most important feature was the swelling of the lamellar phase which in the zwitterionic systems is a result of a hydration force repulsion between the bilayers (3). The existence, as well as many properties of the hydration force are experimentally clearly documented in lecithin-water systems, but the molecular origin of the force is theoretically not yet fully understood. The interface between a lecithin bilayer and water is rather difficult to describe theoretically. The choline groups on the lecithin molecules are not locked in a well defined position as, but they are free both to rotate and to adjust in different angles relative to the interface. Lamellar aggregates formed by octylammonium octanoate and similar compounds are also uncharged and, what is more, they could be easier described theoretically than lecithin bilayers. As a first approximation it may be assumed that the positive and negative headgroups on the octylammonium and octanoate ions, respectively, are located at the same distance from the interface between water and the bilayer of amphiphilic molecules.

The second reason for starting this work was to obtain experimental information on the phase equilibria in a three-component system

containing an ionic amphiphile, water and a third, uncharged component composed of an anionic and a cationic amphiphile. There are only few studies of this kind of systems which contain both an anionic and a cationic surfactant in an aqueous environment (4 - 12).

The aim with the work is then to compare the phase diagram of the new system with earlier very carefully examined phase diagrams of an ionic surfactant, water and a third, uncharged component (13 -17) to obtain a better understanding of how the third component influences the stability of the aggregates and liquid crystals. We have in particular compared the new system with ternary systems containing a long-chained alcohol as the third component to clarify similarities and differences between the two types of systems. The differences in the ability for the formation of reversed micellar structures are of special interest.

We will in this work also use theoretical models for the thermodynamics in ionic amphiphile-water systems in order to obtain a deeper understanding of the molecular origin of different phase behaviours.

A theoretical model that gives a satisfactory description of the thermodynamics and phase equilibria in ionic surfactant - water systems have been developed at this laboratory in a series of papers during the last years (18, 19). The model is also able to predict the phase equilibria in three-component systems containing an ionic surfactant, a long-chained alcohol and water (20). In this work we use a slightly modified version of this thermodynamic model (21) in order to demonstrate the molecular origin of the phase behaviour.

Materials and methods

Sodium octanoate (Na^+A^-), octanoic acid and octylamine were all supplied by BDH and were of more than 97.5 % purity. No further purification was made before use.

Octylammonium octanoate (A^+A^-) was prepared as follows: When two saturated solutions of octanoic acid and octylamine, respectively, in diethylether were mixed in equimolar ratio, octylammonium octanoate precipitated. The salt was then washed with diethylether and dried under vacuum.

The samples were prepared by weighing the compounds into glass tubes which were flame-sealed. The samples were then equilibrated in a thermostated bath at 298 K for at least two days before the first examination. Most of the samples were also reexamined after two years.

About 150 samples were prepared at regular composition intervals over the ternary diagram to obtain a preliminary phase diagram. Additional samples were then made especially at low sodium octanoate concentrations to further clarify the phase behaviour of the system in that concentration range.

The samples were examined preliminarily against crossed polaroids in order to ascertain the homogeneity and the occurrence of birefringency. The liquid crystalline phases were further examined in a polarizing microscope (22).

The results obtained by means of the polarizing microscopy have a good agreement with the observations made with the naked eye (22).

The samples that are classified as a lamellar phase have a semicloudy appearance and they flow slowly under the influence of gravity.

In the microscopy, they show a mosaic pattern as well as oily streaks, which are the most typical textures for a lamellar phase structure.

On the other hand, the samples of the hexagonal phase are more transparent and much stiffer than the samples of the lamellar phase. They can be identified by the nongeometric and angular texture that they are showing in the microscope.

The polarizing microscopy was also used to confirm the existence of crystals and, furthermore, to follow the extension of the isotropic phase (L_2) as a function of temperature.

Samples along the binary axis water-octylammoniumoctanoate were also studied by means of X-ray diffraction (23) in order to clearly determine the types of liquid crystals and phase boundaries along this axis.

The phase diagram at different temperatures.

The boundaries of the one-phase regions in the system at 298 K are shown in Fig. 1. The most notable features of this diagram are:

- i) The resemblance with the phase diagram for the three component system sodium octanoate - decanol - water (13, 16, 17) for octylammonium octanoate concentrations less than 50% w/w.
- ii) In addition to the crystalline surfactants, only three different one-phase regions exist in the system, a normal micellar phase, a normal hexagonal phase and a lamellar phase.
- iii) That the lamellar phase is stable in a small region along the binary axis water - octylammonium octanoate.
- iiii) The increasing swelling of the lamellar phase at the addition of small amounts of sodium octanoate.
- iiiii) The solubility of the octylammonium octanoate in water is very low.

The lamellar phase is at small water concentrations limited by two-phase regions where the lamellar phase is in equilibrium either with sodium octanoate or with octylammonium octanoate crystals. The three-phase triangle containing crystalline sodium octanoate, crystalline octylammonium octanoate and the lamellar phase, that separates the two two-phase regions containing the lamellar phase and sodium octanoate or octylammonium octanoate crystals, respectively, was not determined in the examinations due to experimental difficulties in distinguishing the

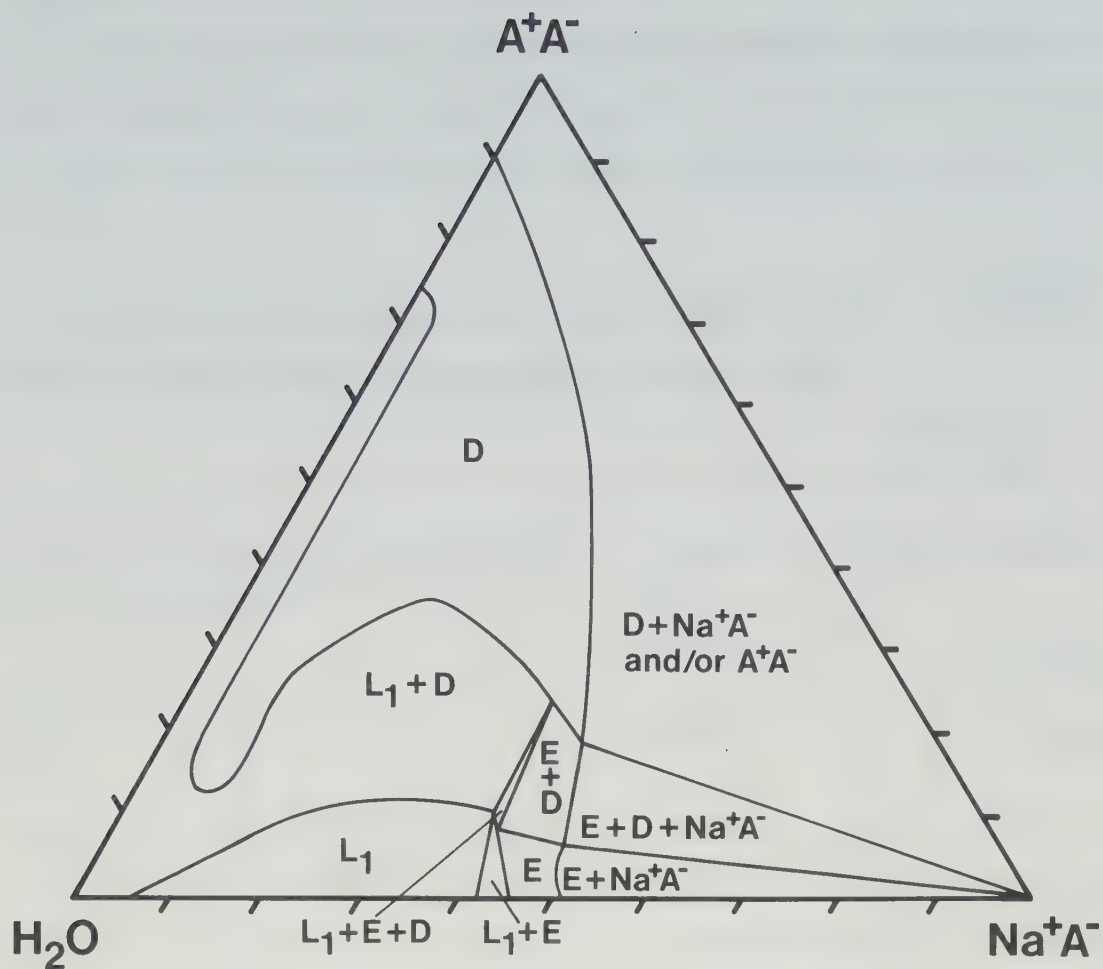


Fig. 1. Equilibrium diagram for the system sodium octanoate (Na^+A^-) - octylammonium octanoate (A^+A^-) - water at 298 K.

L_1 = Region with a homogeneous isotropic solution.

E = Region with a homogeneous hexagonal mesophase.

D = Region with a homogeneous lamellar mesophase.

two different crystals.

The dimensions of the aggregates in the lamellar phase, measured by means of X-ray diffraction, are found in Table 1 for three different compositions along the binary axis water - octylammonium octanoate.

Table I. X-ray diffraction data of the lamellar mesophase in the octylammoniumoctanoate-water system at 298 K

Composition (% w/w)		Volume fraction of amphiphile*	Bragg spacing (Å)	Dimensions in the lamellar mesophase		
A ₊ A ₋	water			2b (Å)	2L (Å)	A _A (Å ²)
74.81	25.19	0.765	25.2	19.3	5.9	25.9
80.00	20.00	0.815	24.7	20.1	4.6	24.9
84.67	15.33	0.860	23.7	20.4	3.7	24.6

* $\rho_{A+A^-} = 0.91 \text{ kg/dm}^3$

The substantial increase in swelling of the lamellar phase when small amounts of sodium octanoate are added is in the phase diagram indicated to occur at a sodium octanoate concentration of around 3% w/w. This concentration may, however, be somewhat lower since the number of samples in our investigation is not big enough to determine the phase boundary within an accuracy higher than 3% w/w.

The phase boundary between the lamellar phase and the octylammonium octanoate crystals is rather temperature dependent as may be seen in the binary phase diagram in Fig. 2. The maximal extension of the lamellar phase occurs at the eutectic point, between 310 and 311 K.

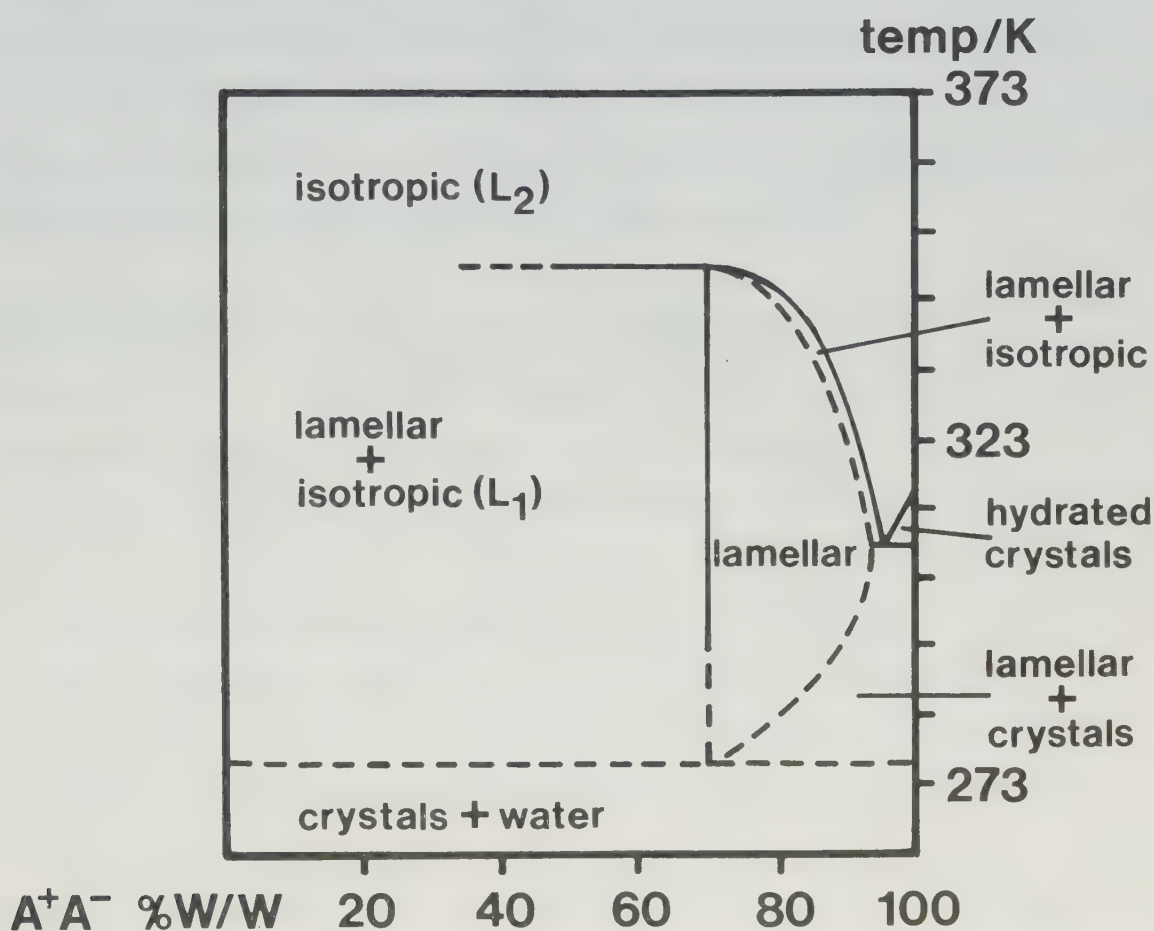


Fig. 2. Phase diagram of the A^+A^- - water system.

The solubilization of sodium octanoate and water in the isotropic bulk phase of octylammonium octanoate starts at temperatures above 310 K as may be seen in Fig. 3. As the isotropic phase starts to form in the octylammonium octanoate corner of the phase diagram at high temperatures, the lamellar phase becomes more and more suppressed.

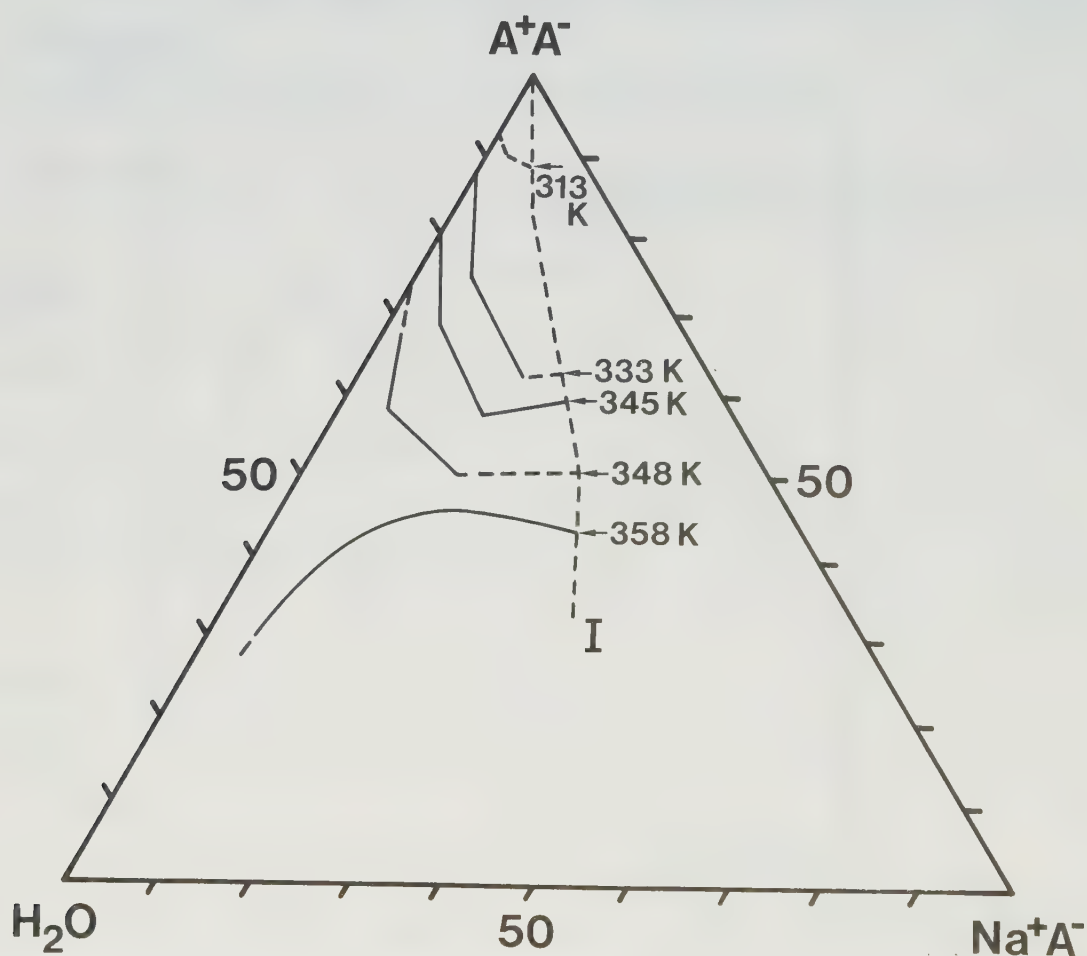


Fig. 3. Phase diagram showing the extension of the isotropic region (L_2) at different temperatures. Line I is the phase boundary against the crystalline phases; the other lines show the phase boundary against the liquid crystalline phase at different temperatures.

A theoretical model for the experimentally studied system.

We will in this part of the work extend a recently presented theoretical model of the thermodynamics of systems containing an ionic amphiphile, a long-chained alcohol and water (20) so that the model also will be able to describe the experimentally studied system. The aim with this theoretical work is to obtain a better understanding of the molecular reasons for the stability of the lamellar phase in the binary system octylammonium octanoate - water and for the tremendous swelling of the lamellar phase when only small amounts of an ionic amphiphile are added.

Most parts of the thermodynamic model used have been presented previously (18 - 21). We will therefore only give a brief summary of the different assumptions in the model and focus on the special new assumptions that must be made to describe the present system.

1. All octylammonium and octanoate ions are for temperatures below the eutectic melting point of octylammonium octanoate and water assumed to be either incorporated in aggregates with the ionic group in the hydrocarbon - water interface, or dissolved in the aqueous part.
2. The number of octylammonium and octanoate ions dissolved in the water part is so low that they may be neglected except for solutions with very high water contents.

3. Counterions are always dissolved in the water part and distributed there according to the Poisson-Boltzmann theory.
4. The aggregates are assumed to be normal or reversed spherical micelles, infinite cylinders packed in a hexagonal lattice or infinite bilayers stacked to a lamellar liquid crystal.
5. An isotropic phase of octylammonium octanoate that possibly may solubilize some water can form at temperatures above the eutectic melting point of octylammonium octanoate and water.

The free energy G of a three component system containing sodium-octanoate, octylammoniumoctanoate and water may according to the model be written as

$$G = n_{\text{H}_2\text{O}} \mu_{\text{H}_2\text{O}}^{\circ} + n_{\text{Na}^+\text{A}^-} \mu_{\text{Na}^+\text{A}^-}^{\circ} + n_{\text{A}^+\text{A}^-} \mu_{\text{A}^+\text{A}^-}^{\circ} + G_s + G_{\text{el}} - TS_{\text{mix}} + G_{\text{disp}} + G_{\text{hf}} \quad (1)$$

where μ_i° is the standard chemical potential of component i , G_s a surface free energy, G_{el} an electrostatic free energy, T the temperature, S_{mix} the entropy from the mixing of the components, G_{disp} the free energy from the dispersion interactions and G_{hf} a free energy responsible for the hydration force.

The surface free energy G_S is assumed to follow the empirical equation (18)

$$G_S = (n_{A^+} + n_{A^-}) * \gamma * A_A \quad (2)$$

where γ is an experimentally determined parameter (18, 20) and A_A the surface area of an amphiphile (the surface area of an octanoate ion is here assumed to be the same as for an octylammonium ion). The contributions to the chemical potentials from the surface free energy will then be

$$\mu_{A^+A^-} = 2 \gamma * A_A \quad (3a)$$

$$\mu_{Na^+A^-} = \gamma * A_A \quad (3b)$$

The contributions to the chemical potentials from the electrostatic free energy G_{el} and the entropy of mixing TS_{mix} will depend on the form and composition of the aggregate in a rather involved way (18). It is only for the lamellar systems that it is possible to obtain simple analytic equations for the free electrostatic energy that easily may be solved without using a computer. We will therefore here only present the chemical potentials for a lamellar system, since we in this investigation mostly deal with lamellar phases. The equations for the chemical potentials for the other phases may be found in ref.(18).

$$\mu_{H_2O} = -kT * c_{Na^+}(0) / 55.5 \quad (4a)$$

$$\mu_{A^+A^-} = kT * \ln(X_{A^+} * (1 - X_{A^+})) - 4 A_A * E_{el}/A \quad (4b)$$

$$\mu_{Na^+A^-} = kT * \ln((1 - X_{A^+}) * c_{Na^+}(L)/55.5) - 2 A_A * E_{el}/A \quad (4c)$$

k is here the Boltzmann constant and $c_{\text{Na}^+}(0)$, $c_{\text{Na}^+}(L)$ the concentrations of the counterion sodium at $z=0$ respectively $z=L$, see Fig. 4. X_{A^+} is the mole fraction of octylammonium ions in the aggregates and E_{el}/A the electrostatic energy per interface area from the ion-ion interaction (18).

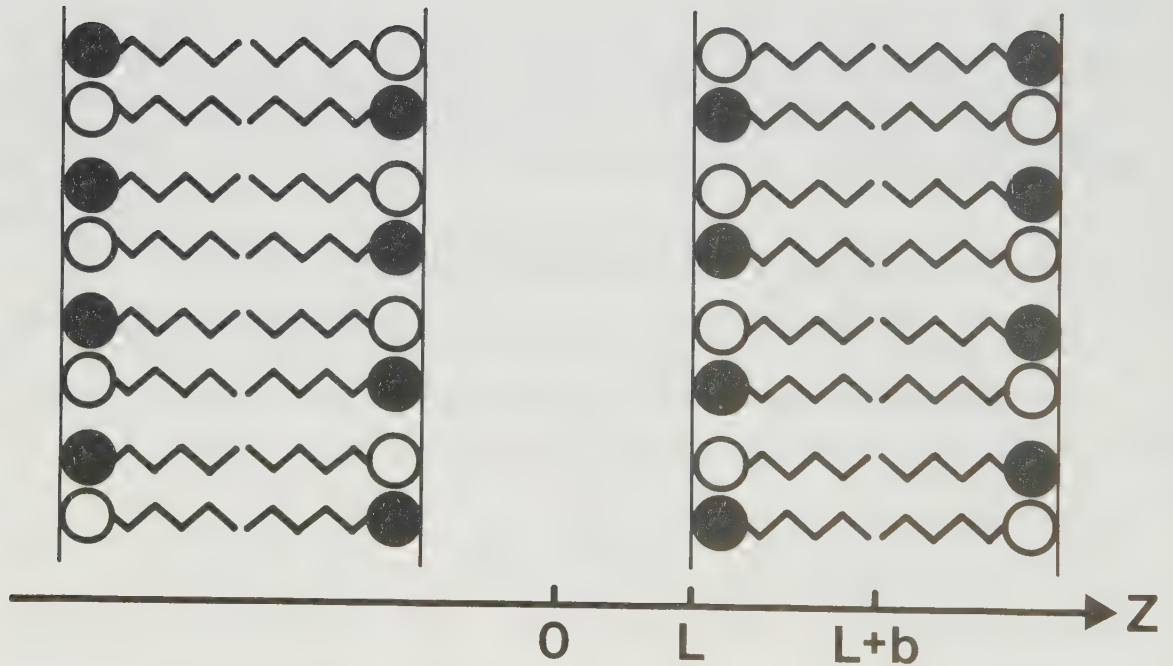


Fig. 4. Schematic representation of a lamellar system. The thickness of the amphiphilic bilayer is $2b$ and the thickness of the water layer is $2L$.

E_{el}/A the electrostatic energy per interface area and the concentrations $c_{Na^+}(0)$ and $c_{Na^+}(L)$ may for a lamellar system be written as (18)

$$A_A * E_{el}/A = kT * (1 - 2X_{A^+}) * (1 - s/\tan s) \quad (5a)$$

$$c_{Na^+}(0)/55.5 = (1 - 2X_{A^+}) * V_{H_2O}/(A_A * L) * s/\tan s \quad (5b)$$

$$c_{Na^+}(L)/55.5 = (1 - 2X_{A^+}) * V_{H_2O}/(A_A * L) * 2s/\sin 2s \quad (5c)$$

where V_{H_2O} is the volume of a water molecule and the parameter s is calculated from

$$s \tan s = K * L * (1 - 2X_{A^+}) \quad (6)$$

K is defined by the equation

$$K = e^2/(2\epsilon_0\epsilon_r kTA_A) \quad (7)$$

where e is the elementary charge, ϵ_0 the permittivity in vacuum and ϵ_r the dielectric constant in water.

The dispersion energy G_{disp} may for an infinite array of water and hydrocarbon sheets be written as (24)

$$\begin{aligned} G_{disp}/A &= -H/48\pi b^2 \sum \{ (1 + 1/y^2 j^2)/(1 - 1/y^2 j^2)^2 - 1 \} / y^2 j^2 \\ &= -kT/A_A * f(y) \end{aligned} \quad (8)$$

where H is the Hamaker constant and $1/y$ the volume fraction of hydrocarbon.

$$y = 1 + L/b \quad (9)$$

The dispersion energy is in eq. (8) assumed to be zero when $L \rightarrow \infty$.

The contributions to the chemical potentials from the dispersion energy may then be written as

$$\mu_{H_2O} = kT * f'(y) * V_{H_2O}/(b * A_A) \quad (10a)$$

$$\mu_{A^+A^-} = 2 kT * (f(y)+(1-y)*f'(y)) \quad (10b)$$

$$\mu_{Na^+A^-} = kT * (f(y)+(1-y)*f'(y)) \quad (10c)$$

A lamellar phase can not be stable if there is no repulsive force acting between two bilayers since the dispersion interaction is attractive. The electrostatic repulsion between charged bilayers is in most cases responsible for the repulsion, but for the electroneutral bilayers in the binary system of octylammonium octanoate and water there must be another repulsive force operating in the system. Since we have no further information about this repulsive force we will here assume that it has the same origin and the same form of the distance dependence as the hydration force between lecithin bilayers (3). The energy contribution due to the hydration force in our system is therefore written as

$$G_{hf}/A = kT * K_{hf}/A_A * \exp(-2L/\lambda) \quad (11)$$

where K_{hf} and λ are empirical constants. The contributions to the chemical

potentials from G_{HF} will then be

$$\mu_{H_2O} = -2kT * K_{hf} * V_{H_2O} / (\lambda * A_A) * \exp(-2L/\lambda) \quad (12a)$$

$$\mu_{A^+A^-} = 2kT * K_{hf} * (1 + 2L/\lambda) * \exp(-2L/\lambda) \quad (12b)$$

$$\mu_{Na^+A^-} = kT * K_{hf} * (1 + 2L/\lambda) * \exp(-2L/\lambda) \quad (12c)$$

The chemical potentials may now be obtained by combining equations (1), (3), (4), (5), (10) and (12).

$$\mu_{H_2O} = \mu^\circ_{H_2O} + kT \{ -b*s^2/(KL^2) + f'(y) - 2K_{hf}*b/\lambda*\exp(-2L/\lambda) \} * V_{H_2O}/(b*A_A) \quad (13a)$$

$$\begin{aligned} \mu_{A^+A^-} = & \mu^\circ_{A^+A^-} + kT * \{ \ln (X_{A^+} * (1-X_{A^+})) - 4*(s \tan s - s^2)/(KL) + \\ & 2*(f(y) + (1-y)*f'(y)) + 2*K_{hf}*(1 + 2L/\lambda)*\exp(-2L/\lambda) \} + \\ & 2*\gamma*A_A \end{aligned} \quad (13b)$$

$$\mu_{Na^+A^-} = \mu^\circ_{Na^+A^-} + (\mu_{A^+A^-} - \mu^\circ_{A^+A^-})/2 + kT * \{ \ln (V_{H_2O}/(KA_A L^2)) * (s/\cos s)^2 - 0.5*\ln (X_{A^+} / (1-X_{A^+})) \} \quad (13c)$$

In applying the equations for the chemical potentials one must know the interfacial area of an amphiphilic molecule A_A as well as the thickness of a hydrocarbon sheet $2b$. These quantities may for systems with low charge densities be calculated from the volume V_A and the maximum length b_{max} of the amphiphilic molecules.

$$b = b_{max} \quad (14a)$$

$$A_A = V_A / b \quad (14b)$$

Equation (14a) may, however, not be used for systems with high charge densities since the repulsion between the charges in a bilayer then is so strong that the area per amphiphile increases in order to reduce the repulsions. Consequently, the bilayer becomes thinner than $2b_{\max}$. The charge density in the lamellar phase of the studied system is however for octylammonium octanoate concentrations above 30% w/w too low to cause a reduction of the bilayer thickness. We will therefore use eq. (13a) as an approximation in all calculations. The condition for optimal size of the bilayer thickness may be found in ref.(18).

The computational procedure

The condition for equilibrium between two phases I and II is that the chemical potentials for all components in both phases should be the same

$$\mu_i^I = \mu_i^{II} \quad i = \text{H}_2\text{O}, \text{A}^+\text{A}^-, \text{Na}^+\text{A}^- \quad (15)$$

A convenient way to obtain a solution to the three equations in (15) is to plot $\mu_{\text{Na}^+\text{A}^-}$ as a function of $\mu_{\text{H}_2\text{O}}$ for constant values of $\mu_{\text{A}^+\text{A}^-}$, as shown in Fig 5. The point in Fig. 5 where the two parts of the curve intersect gives the chemical potentials for the two phases in equilibrium and the corresponding compositions of the phases may then also be calculated.

The process is repeated for different $\mu_{\text{A}^+\text{A}^-}$ values, giving the phase

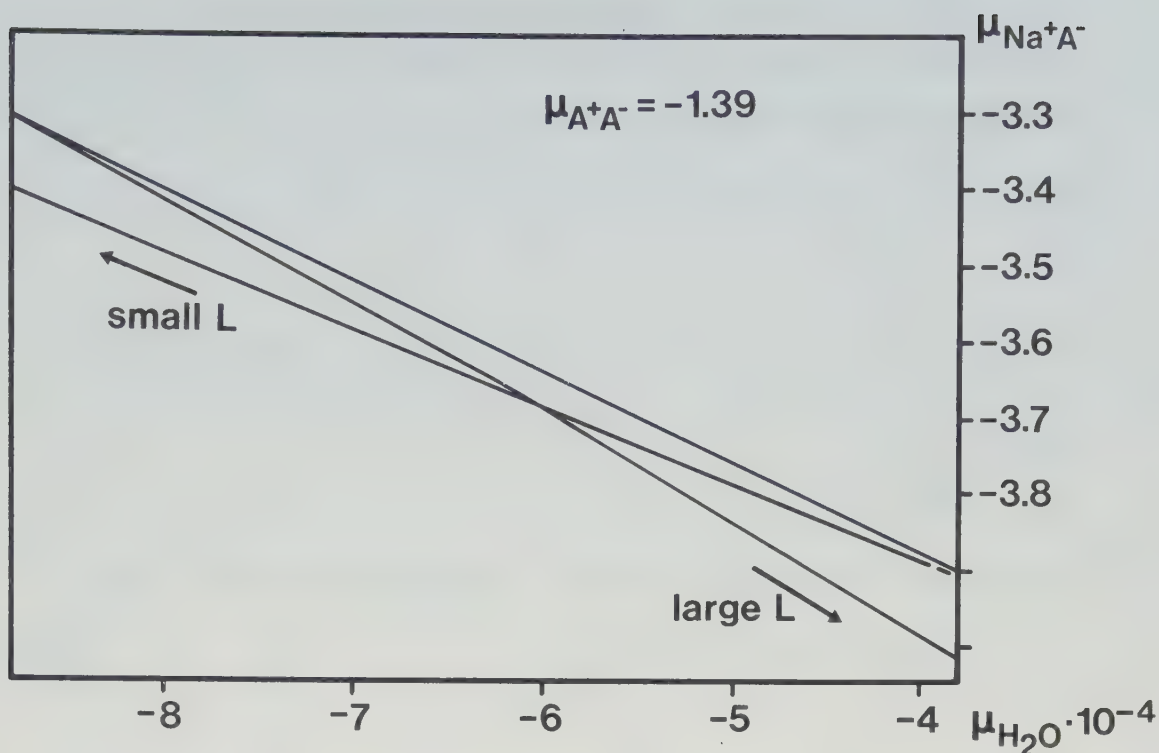


Fig. 5. The chemical potential of sodium octanoate $\mu_{Na^+A^-}$ as a function of the chemical potential of the water μ_{H_2O} in a lamellar mesophase. The temperature is 298 K and the chemical potential of octylammonium octanoate is constant.

equilibria at different compositions, see Fig. 6. In this diagram, the weight fraction of the ionic surfactant is plotted as a function of the water layer thickness. At low ($<1\%$ w/w) Na^+A^- concentrations, there is a two-phase region between two lamellar phases with different water contents. Tie-lines are drawn between the two compositions which are in equilibrium with each other.

The greatest problem in the computational scheme is to find the X_{A^+} values that for different L values keep the chemical potential of octylammonium octanoate constant. A considerable simplification may however be obtained if X_{A^+} in eq. (13a) is replaced by the s parameter from eq. (6). The condition for constant $\mu_{A^+A^-}$ is then given by eq. (17)

$$\ln(1-(s \tan s / (K \cdot L))^2) - 4(s \tan s - s^2)/(K \cdot L) = K^2 \quad (17)$$

where

$$K^2 = (\mu_{A^+A^-} - \mu^\circ_{A^+A^-} - 2 \cdot \gamma \cdot A_A) / kT - 2 \cdot (f(y) + (1-y) \cdot f'(y)) - 2 \cdot K_{hf} \cdot (1 + 2L/\lambda) \cdot \exp(-2L/\lambda) + \ln 4 \quad (18)$$

The following stepwise procedure is used in the calculations:

1. Choose a value for the chemical potential difference $\mu_{A^+A^-} - \mu^\circ_{A^+A^-}$
2. Choose a value for the thickness of the water layer $2L$
3. Calculate K^2 from eq. (18)
4. s may now be obtained from eq. (17) for example by Newton-Raphsons method for solving nonlinear equations.
5. X_{A^+} is calculated from eq. (6)
6. $\mu_{Na^+A^-}$ and μ_{H_2O} are calculated from eqs. (13a) and (13c)
7. The procedure from 2. to 6. is repeated with different L -values until a diagram like Fig. 5 is constructed.

8. The process from 1. to 7. is repeated for new values of $\mu_{A^+A^-}$ - $\mu_{A^+A^-}^*$ until a complete phase diagram like the one in Fig. 6 is constructed.

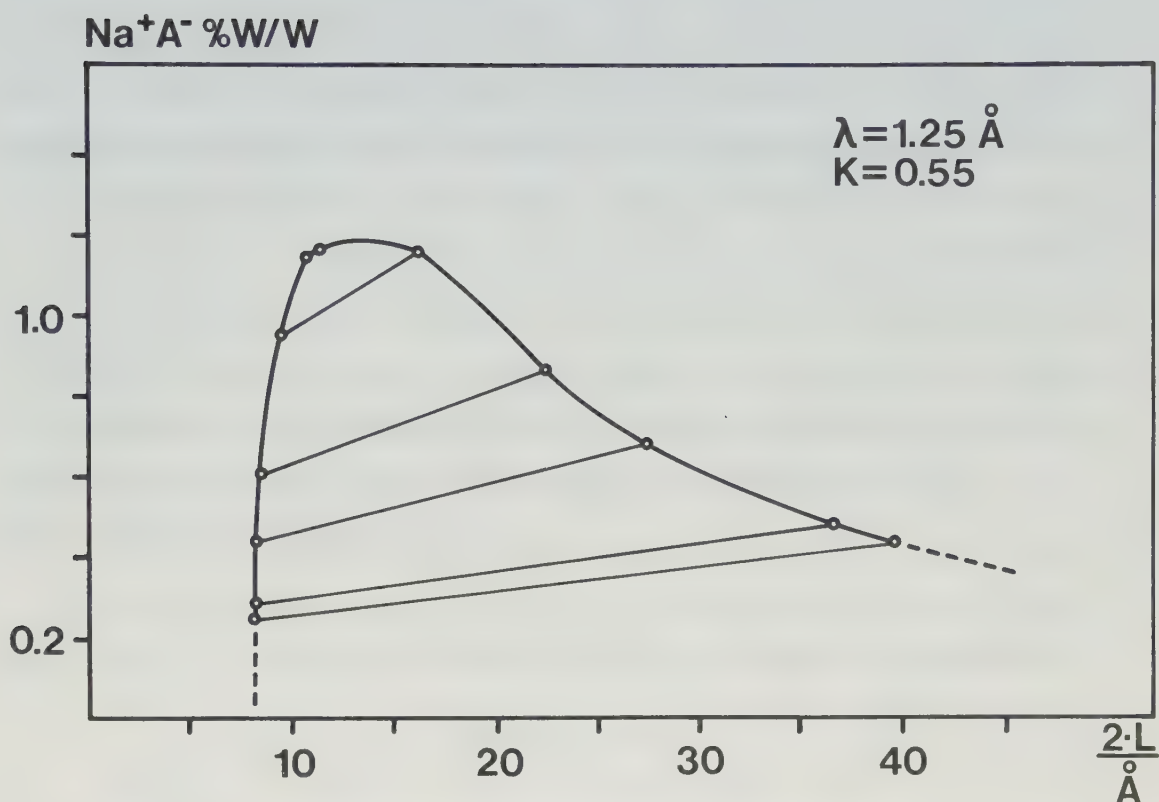


Fig. 6. Calculated phase equilibria for the lamellar mesophase of the Na⁺A⁻ - A⁺A⁻ - water system at 298 K.

Results and discussion

The binary system octylammonium octanoate water shows properties that may be highly relevant for the understanding of the hydration force phenomena in zwitterionic amphiphilic systems. It is for a lamellar system of zwitterionic amphiphiles, like lecithin, well known that a strong repulsive force starts to operate at lamellar separations shorter than 30 Å (3). The molecular origin of the force is still under debate (25). A lot of theoretical work has been done to understand the force, but most of the proposed models are rather crude and contain unknown parameters that are not known for the lecithin - water system (25). One of the problems that occur when trying to describe the lecithin - water system is that the interface between water and lecithin is rather difficult to describe theoretically and it seems that the hydration force is sensitive to interfacial conditions. Also for a normally such a powerful method as the Monte Carlo simulation technique the system seems to be tricky. The main problem is to obtain a proper description of the electrostatic interactions between the choline-groups in a relatively large interfacial domain where the electrostatic polarisability of the medium may be rather different from what it is in a water or hydrocarbon region .

Lamellar systems of symmetrical amphiphilic salts (A^+A^-) such as octylammonium octanoate, may be more suitable than lecithin for testing theoretical models of the hydration force since the interface between an A^+A^- bilayer and water is more well-defined.

It is not possible from our experimentally obtained phase diagram to determine both parameters in the equation for the hydration force assumed here eq.(11). The strength of the hydration force at the maximum uptake of water between the bilayers may be obtained from the equation for the

dispersion force, eq.(8), since there is a balance between the repulsive hydration force and the attractive dispersion force at that distance between the bilayers. From Table 2 it is clear that either the hydration force for the octylammonium octanoate system is considerably weaker than the corresponding force in lecithin systems for all distances (K_{hf} for lecithin ≈ 10), or that the decay length of the force is less than 1 Å in the octylammonium octanoate system which can be compared with the 2.5 Å decay length found in the lecithin water system. If the later suggestion is true the system seems to be more like the phosphatidylethanolamine - water system where a hydration force with a decay length between 1 and 1.5 Å has been found (3).

Table II.

The maximum swelling of the lamellar mesophase in the octylammoniumoctanoate-water system as a function of the strength of the hydration force.

K_{hf}	λ (Å)	maximum swelling (% w/w H ₂ O)	water layer thickness (Å)
0.55	1.25	31	8.0
5.5	1.25	42	12.5
55	1.25	49	17.0
5.5	0.8	29	7.0
5.5	1.5	48	16.0
5.5	2.0	57	23.5

The phase diagrams of other A^+A^- systems where the headgroup of the A^+ molecule is made more bulkier, for example by substituting the ammonium ion by a trimethylammonium ion, has also been studied in our laboratory and the results will be reported in elsewhere. It is, however, interesting to note that the hydration force becomes considerably more long ranged and similar to the one in the lecithin-water system for A^+A^- systems with bulkier headgroups. This observation indicates that the A^+A^- systems behave very much like the zwitterionic systems, provided that the headgroups of the amphiphilic molecules in the A^+A^- system resemble the positive and negative groups in the zwitterionic headgroups.

Theoretical calculations of phase equilibria leads to a better understanding of the thermodynamics in the system. The rather remarkable increase in the lamellar swelling when only small amounts of sodium octanoate are added is an example of this. The theoretical phase diagram in Fig. 6 predicts that the demixing gap that exists in the lamellar phase disappears at such a small sodium octanoate addition as less than 1% w/w. The reason for the demixing gap is according to the model the attractive dispersion force between the bilayers. Since the dispersion force is rather weak in hydrocarbon - water systems (the Hamaker constant is less than $6 \cdot 10^{-21}$ J) compared to the electrostatic forces in ionic lamellar systems (18), only small amounts of ionic amphiphile are needed to produce an electrostatic repulsion between the bilayers that is comparable with the attractive dispersion force.

An interesting peculiarity for octylammonium octanoate is the relatively low melting point of the salt, 315 K, which gives a rather pronounced effect on the phase diagram above this temperature. The lamellar phase is in the binary system octylammonium octanoate - water totally replaced by

an isotropic phase at 348 K as may be seen in Fig. 2.

The solubility of sodium octanoate and water is rather high in the isotropic phase as may be seen in Fig. 3. It seems that water, sodium octanoate and octylammonium octanoate may form reversed micellar structures in a continuous bulk phase of octylammonium octanoate, in much the same way as for corresponding systems where octylammonium octanoate is replaced by a long-chained alcohol (13, 16, 17).

Further work is going on in our laboratory to obtain a better understanding of the thermodynamics in different A^+A^- systems. The experimental work is concentrated on obtaining phase diagrams for A^+A^- systems with different A^+ and A^- headgroups, but the solubility of long-chained alcohols and other molecules in different A^+A^- - water systems is also investigated. The results may be helpful to clarify the molecular origin of the hydration force, but they may also become useful for technical applications.

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**Phase equilibria of
catanionic surfactant - water systems**

by

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ABSTRACT

In this work, we have studied the phase equilibria of binary amphiphilic -water systems, where the amphiphilic molecule is composed of a cationic (A^+) and an anionic (A^-) surfactant in equimolar ratio, and the inorganic counterions are eliminated (catanionic surfactant). The studied catanionic compounds are: dodecylammonium dodecanoate, dodecylammonium dodecylsulphate, dodecyltrimethylammonium dodecylsulphate and dodecylethyldimethylammonium dodecylsulphate. As all the ionic surfactants have approximately the same solubility in water the electrostatic effects in the system can be neglected.

Below 373 K, the catanionic surfactant -water systems show similar phase behaviour as lecithin - water systems, where a lamellar phase is in equilibrium with almost pure water. In both cases, the swelling of the lamellae is assumed to be due to the hydration force interactions between the bilayers. However, due to the structure of the polar headgroup, the catanionic systems are easier to describe in theoretical model studies of hydration force than the zwitterionic phospholipid systems.

The experimental results show that the strength of the hydration force is more dependent on the size of the polar headgroups than the specific chemical composition of them. Furthermore, no hydrophobic attraction could be observed between the bilayers.

The results are also discussed in light of some main theories that are suggested for the repulsive hydration force and the attractive hydrophobic interaction.

INTRODUCTION

The phase equilibria of many different anionic and cationic amphiphiles in an aqueous solution have been studied in great detail, both experimentally (1) and theoretically (2 - 4), but there are only few studies of systems where both a cationic and an anionic surfactant are mixed with water (5 - 13). This kind of systems can, however, show very interesting phase behaviour as we have already observed in the studies of the ternary system octylammonium octanoate - sodium octanoate - water (14).

In this work, we have studied four different binary systems with an amphiphilic compound, composed of a cationic (A^+) and an anionic (A^-) surfactant in equimolar ratio, mixed with water. Henceforth, we are going to refer to these kind of amphiphiles as catanionic surfactants. In order to be sure that surface charge density of the aggregates in the system can be neglected, the inorganic counterions, if any, are eliminated and, furthermore, all the surfactants used have approximately the same solubility in water. The four catanionic amphiphiles are:

dodecylammonium dodecanoate (AD), dodecylammonium dodecylsulphate (AS), dodecyl- trimethylammonium dodecylsulphate (TAS) and dodecylethyldimethyl- ammonium dodecylsulphate (EDAS).

The double-chained catanionic surfactants have a similar chemical composition as zwitterionic phospholipids, such as lecithin or phosphatidyl-ethanolamine, and from the studies of the ternary system octylammonium octanoate - sodium octanoate - water (14) we know that the phase behaviour of binary catanionic surfactant - water systems is, indeed,

parallel to that of a lecithin - water system (15 - 22).

Both systems form a lamellar phase which is in equilibrium with almost pure water through a relatively large two-phase region (Fig. 1).

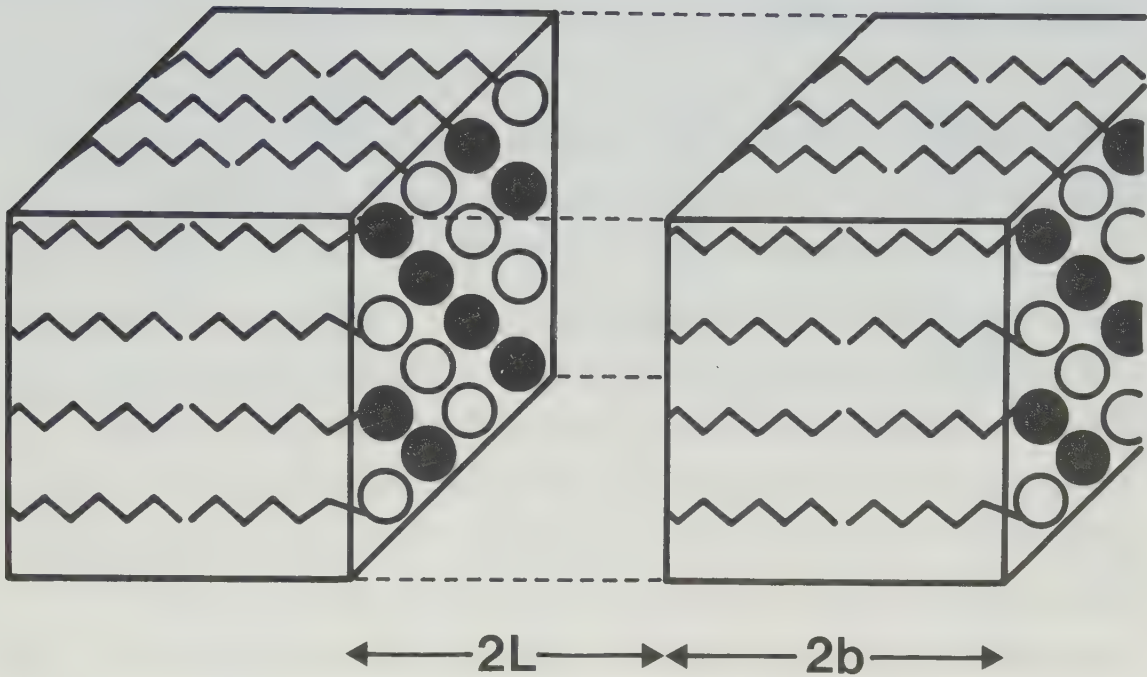


Fig. 1. A schematic representation of the lamellar phase. $2 \times L$ is the thickness of the water layer and $2 \times b$ is the thickness of the hydrocarbon layer.

As the lamellar aggregates are uncharged the existence of the swollen bilayer structure can only be explained if there is another repulsive force operating between the bilayers than the electrical double-layer repulsion. In lecithin - water systems, the additional force is proposed to be the so called hydration force (23 - 32), so that it is assumed that the hydration force is responsible for the swelling of the lamellae also in catanionic surfactant - water systems.

The aim with this work has been to further investigate the effect of the polar headgroup on the interactions between the lamellar bilayers. Therefore, the size of the headgroup of the four studied catanionic surfactants is systematically increased.

The advantage of studying the bilayers that are formed by catanionic molecules is that we can assume that both the positive and negative headgroups are lying at the same distance from the hydrocarbon surface, while choline groups of a zwitterionic lecithin molecule are able to rotate relatively freely (Fig. 2). Therefore, catanionic surfactant - water systems should be more suitable for theoretical model studies of the hydration force.

The experimental results are also discussed in light of the main theories that are suggested for the repulsive hydration force on one hand (33 - 44), and the attractive hydrophobic interactions on the other hand (42 - 48).

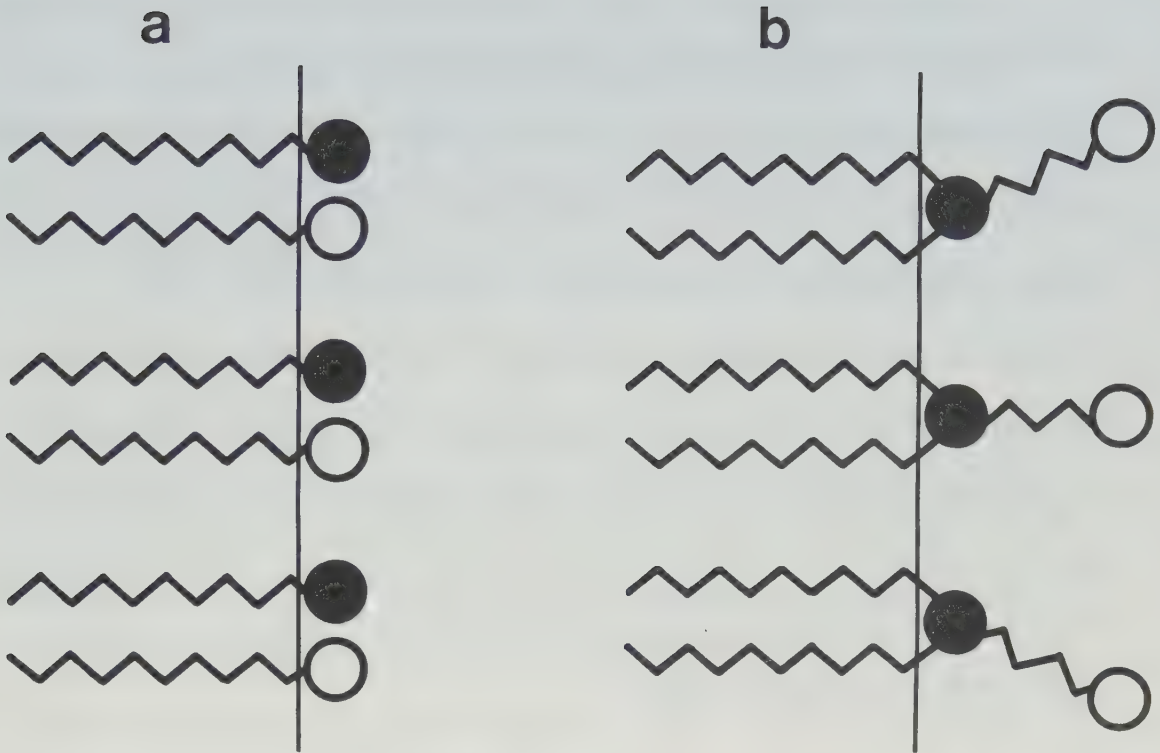


Fig. 2. Orientation of the polar headgroups relative to the hydrocarbon surface. A schematic representation of
a) an catanionic system
b) a zwitterionic phospholipid system.

MATERIALS

The initial cationic surfactants are dodecylamine ($R_{12}NH_2$), dodecyltrimethylammonium bromide ($R_{12}N(CH_3)_3Br$) and dodecylethyl-dimethylammonium bromide ($R_{12}NC_2H_5(CH_3)_2Br$), and the anionic surfactants are sodium dodecylsulphate ($R_{12}SO_4Na$, SDS) and dodecanoic acid ($R_{11}COOH$, lauric acid). $R_{12}NH_2$ (98%) was obtained from Aldrich-Europe, Belgium; $R_{12}N(CH_3)_3Br$ from Sigma, USA; and $R_{12}NC_2H_5(CH_3)_2Br$ (>98%) from Fluka, Switzerland. Both SDS and lauric acid (specially pure) were obtained from BDH, England. The heavy water (99.7%) was obtained from Merck, Germany. All these chemicals were used without further purification.

The catanionic surfactants were prepared in three different ways:

1) TAS and EDAS

Equivalent amounts of SDS and $R_{12}N(CH_3)_3Br$ (or $R_{12}NC_2H_5(CH_3)_2Br$), respectively, were dissolved in water and the solutions were mixed. TAS (or EDAS) was extracted from the water phase by shaking it with the same volume of diethylether in a separatory funnel at room temperature. The white TAS (or EDAS) -crystals were obtained from the ether phase by distilling off the solvent with a rotavapor. The product was recrystallized in diethylether.

2) AD

Equivalent amounts of lauric acid and $R_{12}NH_2$, respectively, were dissolved in diethylether. When these solutions were mixed AD was precipitated spontaneously. The white AD crystals were collected by means of a suction filtration, and washed with diethylether. AD was dried under reduced pressure.

3) AS

AS was prepared by an cation-exchange method. A solution of SDS was run through a column filled with the resin Amberlite IR-120 (BDH) in its hydrogen form. The acidic eluate was standardized by titrating a portion of the solution with NaOH solution using phenolphthalein as an indicator. $R_{12}NH_2$ was dissolved in ethanol and the solution was neutralized by $R_{12}SO_4H$. The experimentally determined end point had a good agreement with the calculated stoichiometric end point. After neutralization, the AS crystals were collected by means of a suction filtration. In order to remove the possible coprecipitate of $R_{12}NH_2$, the product was washed with diethylether. AS was dried under reduced pressure.

The percentage yield as well as the analytical and physical data for the different catanionic surfactants is given in Table 1.

Table I: Physical and analytical data for the catanionic (A^+A^-) molecules

A^+A^-		melting point / K			
AD		345			
AS		353			
TAS		428			
EDAS		418			

A^+A^-	found %			
	C	H	N	S
AD	74.9 - 75.2	13.6 - 13.7	3.55 - 3.57	-
AS	63.4 - 63.7	11.8 - 12.0	3.15 - 3.19	-
TAS	65.6	12.3 - 12.4	2.89 - 2.94	6.44 - 6.45
EDAS	66.0 - 66.2	12.2 - 12.5	2.75 - 2.79	6.21 - 6.31

A^+A^-	calculated %			
	C	H	N	S
AD	74.7	13.3	3.63	-
AS	63.8	11.8	3.10	-
TAS	65.7	12.0	2.84	6.49
EDAS	66.2	12.1	2.76	6.31

It is of great importance that the catanionic crystals contain equal amounts of positively and negatively charged groups since an unbalanced charge could give rise to an electrostatic repulsion between the lamellar bilayers. An estimation of the upper limit of the net charge was made by a conductivity measurement (49).

The ionic surfactant was extracted from the TAS crystals by mixing about 5 weight per cent of crystals with water. The conductivity of the water phase was then measured. In order to approximate the maximum concentration of the ionic surfactant, we assume that the dominating contributions to the conductivity in the water solution are from Na^+ and Br^- ions. Furthermore, as the total ionic concentration is very low we also approximate the molar conductivity, Λ_m , with the limiting molar conductivity Λ_0 (49). The total concentration of ions in the water phase then becomes:

$$c_{\text{ionic}} = 8 \times 10^{-5} \text{ M} \quad (1)$$

If we assume, for example, that the concentration of SDS is much larger than the concentration of $\text{R}_{12}\text{N}(\text{CH}_3)_3 \text{ Br}$ in water

$$c_{\text{ionic}} \approx c_{\text{SDS}} \quad (2)$$

we obtain an approximation for the maximum concentration of the ionic surfactant in weight percent:

$$X_{\max} \approx 0.04 \% \text{ w/w SDS} \quad (3)$$

This concentration is already so small that the electrostatic effects in the system can be neglected (14). In practice, the concentration may be at least one order of magnitude smaller, as it is not probable that the anionic surfactant would have such a high concentration compared with the cationic surfactant.

THE SAMPLE PREPARATION

The samples consist of two components: one of the four catanionic surfactants and heavy water, and were prepared by weighing the two components directly in glass ampoules which were flame sealed. The samples were mixed by warming to 323 K and repeated centrifugation. They were equilibrated at 323 K at least one week before the first NMR measurement was made. The mixing of samples was repeated and the second NMR measurement was carried out after another two weeks. No significant difference in the NMR measurements was observed.

The same samples were also studied by polarizing microscope. Because of the risk of the decomposition at higher temperatures the samples were stored at room temperature after the thermodynamic equilibrium was achieved.

METHODS

NMR - TECHNIQUE

^2H NMR method has successfully been used to experimental studies of the phase equilibria in several amphiphilic systems (50 - 60). When the water in the system is displaced by heavy water the deuteron quadrupole splittings can give information of water that is incorporated in liquid crystals. What is more, ^2H NMR is a convenient method for determining the boundaries between one-phase and two-phase regions because it is possible to detect very low concentrations of an isotropic phase.

The theoretical background of the NMR-technique is described in detail in several references (61 - 64), therefore, a very brief summary of the theory is given here:

When a nucleus with a non-zero spin quantum number (I) is placed in an external magnetic field the nuclear spin energy consists of ($2I+1$) equidistant energy levels. If the spin quantum number of the nucleus is >1 the nucleus also possesses an electric quadrupole moment. Interaction between the quadrupole moment and an electric field gradient in the nuclear environment displaces the spin energy levels so that the NMR absorption splits into $2I$ separate bands. The interaction is, however, also dependent of the molecular orientation relative to the magnetic field: In an isotropic solution, where all the directions have the same probability, the interaction is averaged to zero by the rapid molecular motion.

Therefore, only a single sharp peak is observed. In an anisotropic liquid crystalline phase, the quadrupole interaction may not be averaged to zero,

and then the frequency signal splits into 2I equally intense peaks. The quadrupole splitting is measured as the distance between the two peaks in frequency units, as shown in Fig. 3a.

If both an anisotropic and an isotropic phase are present, the NMR spectrum is a superposition of the two different spectra because the deuteron exchange between the phases is slow. Thus the spectrum consists of a doublet and a central singlet, Fig. 3b. In the same way, if the sample contains two different anisotropic phases, e.g. a lamellar phase and a hexagonal phase, two doublets will be observed.

^2H NMR study was made at a resonance frequency of 39.14 MHz on a home-built Fourier transform spectrometer equipped with an Oxford Instrument 6-T wide-bore superconducting magnet. The spectra were recorded in the temperature range 328 - 358K. The [12 mm (i.d.)] NMR tube containing the sample ampoule was placed in the NMR probe and the temperature at the airflow around the sample was regulated by means of a variable temperature control unit. The temperature was also checked by means of a copper-constantan thermo couple. The samples were thermally equilibrated several hours before the spectrum was recorded.

POLARIZING MICROSCOPY

The polarizing microscopy studies were used as a supplementary method in

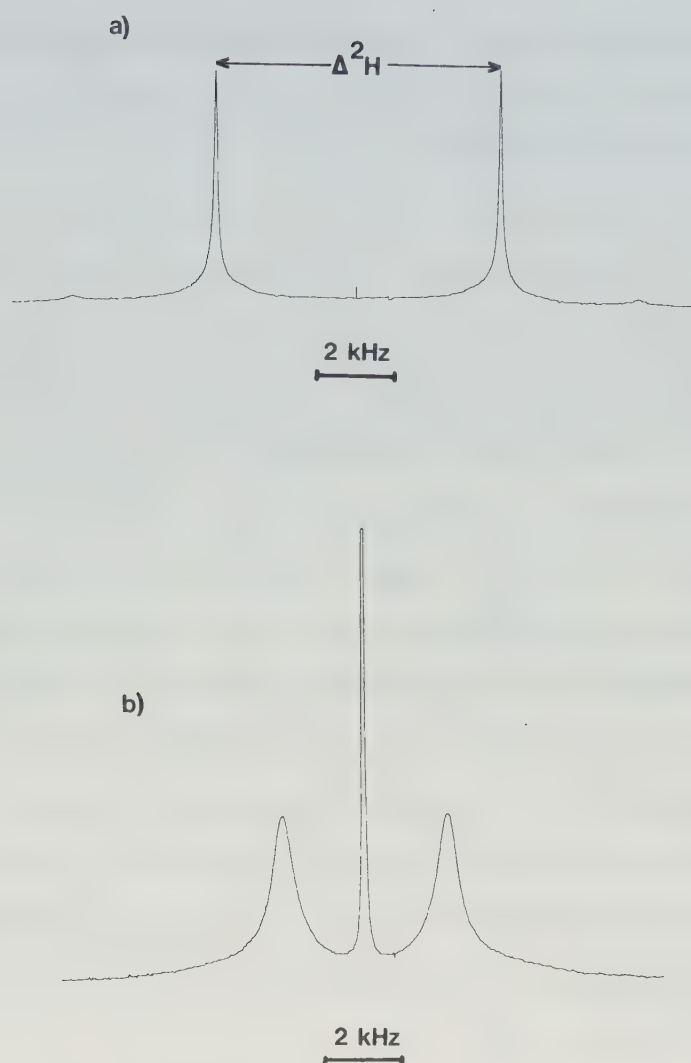


Fig. 3. A deuteron NMR spectrum showing

- a) a quadrupole splitting, Δ^2H (a sample of AD: 13.29 % w/w D_2O , $T = 328\text{ K}$)
- b) both a quadrupole splitting and a central singlet (a sample of AS: 21.89 % w/w D_2O , $T = 328\text{ K}$).

order to confirm the structure of liquid crystalline phases and to detect crystals. The lamellar phase structure was easily identified by a mosaic texture showed in the microscope (65).

An alternative way of determining the phase-boundary between the lamellar phase (D) and the two-phase region (D + L₁) is to apply the two-site model (63, 66). According to the model, there are two types of water binding sites: the "bound" water molecules are bonded to the amphiphilic surface, while the bulk molecules are called "free" water. The exchange rate between the different sites is assumed to be fast.

Furthermore, it is assumed that when water is added to the lamellar system, the dimensions of the amphiphilic aggregates remain unchanged while the amount of free water is changed. This kind of one-dimensional swelling is especially common among non-ionic amphiphiles (67).

The deuteron quadrupole splitting , Δ_D , can then be written as an average of the splittings at the two sites:

$$\Delta_D = | P_f \Delta_f + P_b \Delta_b | = | \Delta_f + n * X_A / X_D * (\Delta_b - \Delta_f) | \quad (4)$$

where the subscripts f and b denote free and bound states; P is the fraction of deuterons, Δ is the quadrupole coupling constant and S is the order parameter; X_A and X_D are the mole fractions of amphiphile and water, respectively, and n is the average hydration number of the

amphiphile. The equation shows that if Δ_D is plotted as a function of X_A / X_D , the plot should be a straight line with a slope $n * (\Delta_D - \Delta_f)$ and an intercept Δ_f . On the other hand, in the two-phase region the deuteron splittings are constant. The intersection of the one-phase line and the two-phase line should then give the X_A / X_D value at the phase-boundary. In Fig. 4, the deuteron splittings are plotted as a function of X_A / X_D for some different catanionic systems.

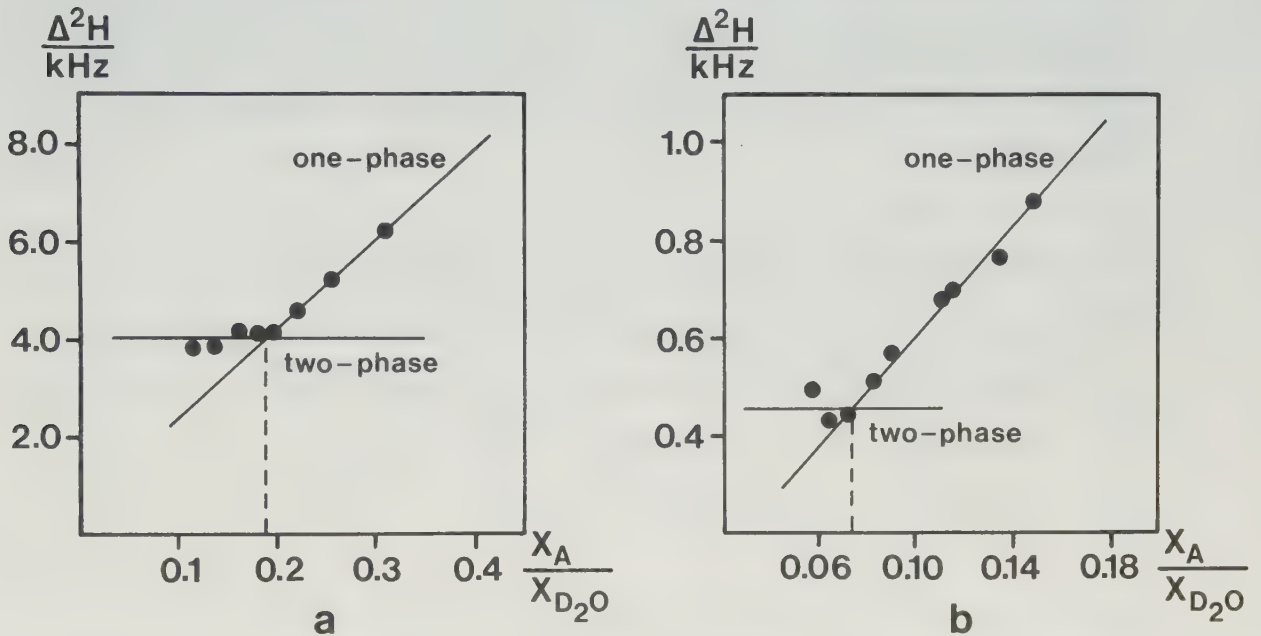


Fig. 4. A plot of Δ^2H as a function of X_A / X_{D_2O} . The phase boundary is obtained at the intersection between the two lines.

a) AS -system at $T = 328$ K

b) EDAS -system at $T = 328$ K.

RESULTS

The four binary phase diagrams for the different catanionic surfactant - water systems are shown in Fig. 5. They have a very similar overall appearance with each other, and also with the binary phase diagram of octylammonium octanoate - water (14).

Above the Krafft temperature, only one liquid crystalline phase, the lamellar phase, is present. As the solubility of the catanionic molecules in water is very low, the lamellar phase is in equilibrium with almost pure water through a large two-phase region. Above a certain temperature, the systems become isotropic. At low water contents, the bulk solution in this isotropic phase is melt surfactant which is able to dissolve water to some extent.

The Krafft temperature decreases with increasing size of the polar head-group: it is 303 K for the EDAS system; 308 K for the TAS system and 318 K for the AS and AD systems. On the other hand, the temperature above which the system turns isotropic is 358 K for the AD system and about 383 K for the three other systems.

The most important feature in the phase diagrams is, however, the swelling of the lamellar phase. As can be seen from the phase diagrams, the maximum uptake of water is 19% w/w $^2\text{H}_2\text{O}$ for the AD and AS systems, whereas the corresponding water concentration is 30% w/w $^2\text{H}_2\text{O}$ for the TAS system and 35% w/w $^2\text{H}_2\text{O}$ for the EDAS system.

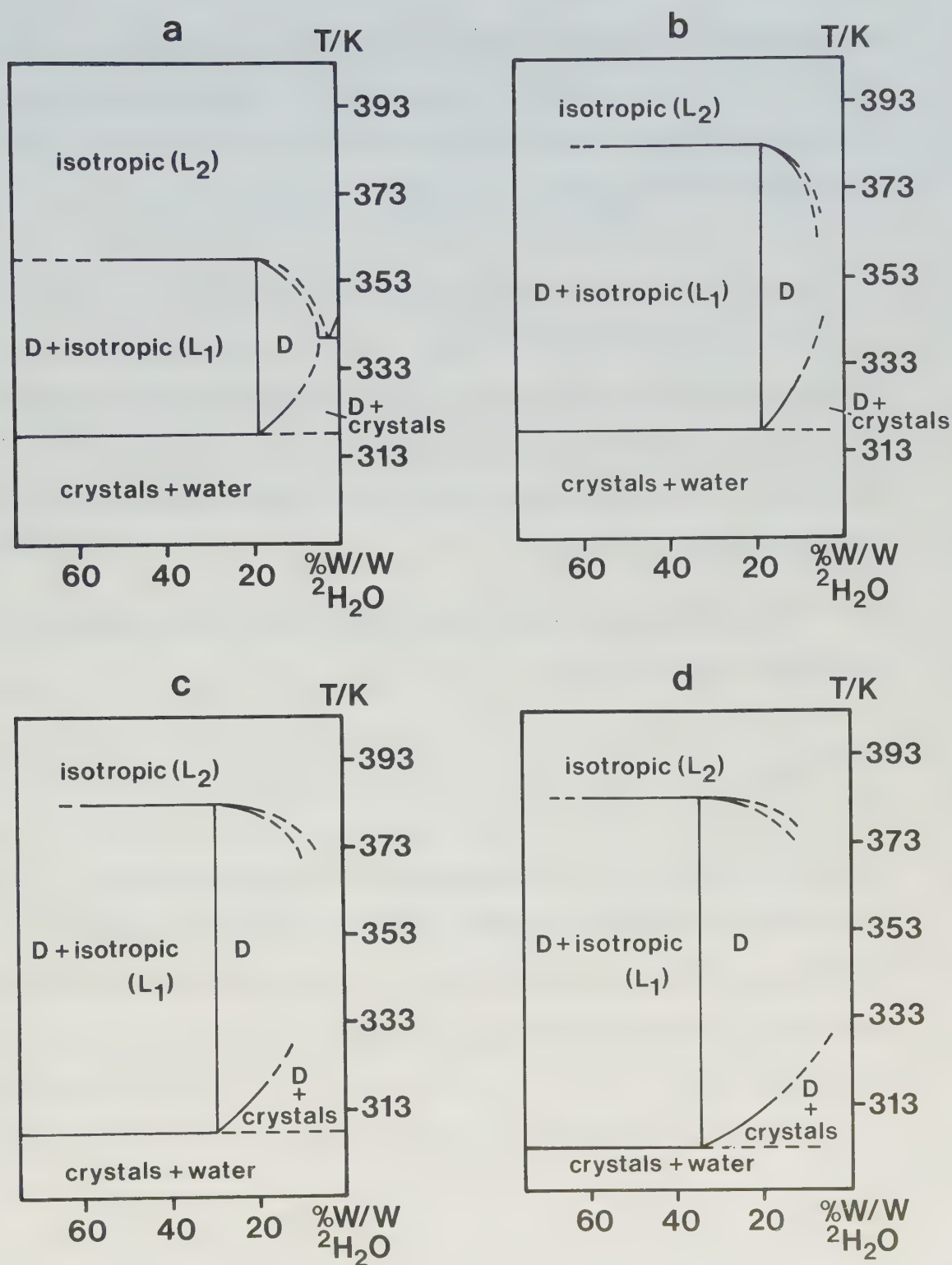


Fig. 5. The experimental phase-diagrams for the four binary cationic systems: a) AD, b) AS, c) TAS and d) EDAS.

We can easily calculate the corresponding water layer separations ($2 \cdot L$, see Fig. 1), if we assume the following model for the lamellar system: When the catanionic molecules are incorporated in a lamellar aggregate, the length of the hydrocarbon chains, b , is

$$b = b_{\max} \quad (5)$$

This approximation is valid in systems with low charge densities where the repulsion between the charges is not able to reduce the bilayer thickness (14). Consequently, it should be a good approximation in the uncharged catanionic systems.

The volume of the water layer (V_{D2O}) and the amphiphilic layer (V_a), respectively, can be written as

$$V_{D2O} = A \cdot L \quad V_a = A \cdot b \quad (6)$$

where A is the surface area for one catanionic molecule which is incorporated in a lamellar aggregate. When the densities of the water layer, ρ_{D2O} , and the amphiphilic layer, ρ_a , are known the thickness of the water layer can be calculated from the equation

$$2 \cdot L = 2 \cdot b \cdot \rho_a / \rho_{D2O} \cdot [1 / (1/X_{D2O} - 1)] \quad (7)$$

where X_{D2O} is the weight fraction of water.

We assume following values for the thickness of the hydrocarbon layer (68) and the densities:

$$b = 16 \text{ \AA} \quad \rho_a = 0.9 \text{ kg/dm}^3 \quad \rho_{D2O} = 1.11 \text{ kg/dm}^3 \quad (8)$$

The resulting maximal water layer thicknesses are: 6.0 Å for the AD and AS systems; 11Å for the TAS system and 14 Å for the EDAS system. The maximum swelling of the lamellar phase in the octylammonium octanoate system which was determined by means of X-ray diffraction (14), was 5.9 Å which has a good agreement with the values obtained from the equation (7).

The maximum swelling of the lamellar phases increases slightly with increasing temperature. As the effect is only 1 - 2 % w/w $^2\text{H}_2\text{O}$ it can hardly be observed in the phase-diagrams, where the phase-boundary between the lamellar phase and the the two-phase region looks like a straight vertical line. The effect of the temperature on the stability of the lamellar phase can, however, be observed from the deuteron NMR spectra. This is shown in Fig. 6 where the NMR-spectrum for the same sample (AD, 20.27 % w/w $^2\text{H}_2\text{O}$) is recorded at three different temperatures. The intensity of the isotropic peak in the spectrum decreases rapidly with increasing temperature, and it has nearly vanished at 348 K.

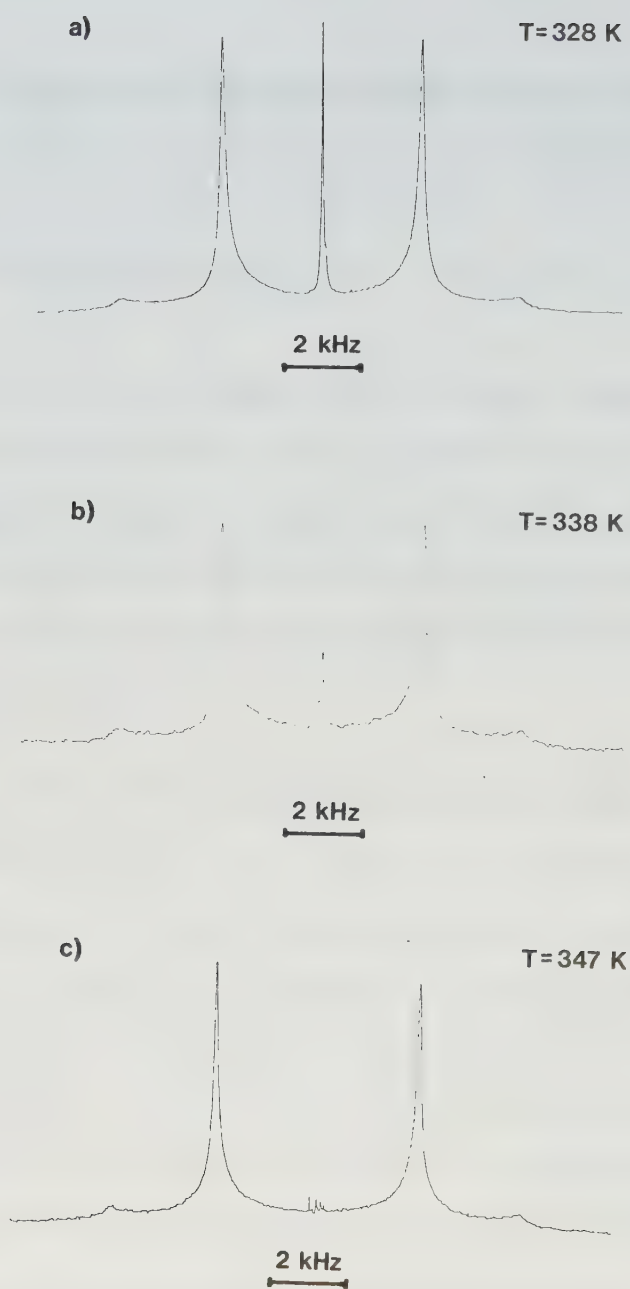


Fig. 6. An AD -sample (20.27 % w/w D_2O) observed at three different temperatures: a) $T = 328$ K, b) $T = 338$ K and c) $T = 347$ K.

The studied catanionic systems can be divided into two groups according to the deuteron splittings observed for the lamellar mesophase. The AD and AS systems show relatively large splittings, 5 - 7 kHz, while the splittings in the TAS and EDAS systems are smaller than 1 kHz. It was also observed that the large deuteron splittings of the AD and AS systems were increasing when the temperature was increased from 328 K to 358 K (Fig. 7a). On the contrary, the smaller splittings of the TAS and EDAS systems decreased with increasing temperature (Fig. 7b).

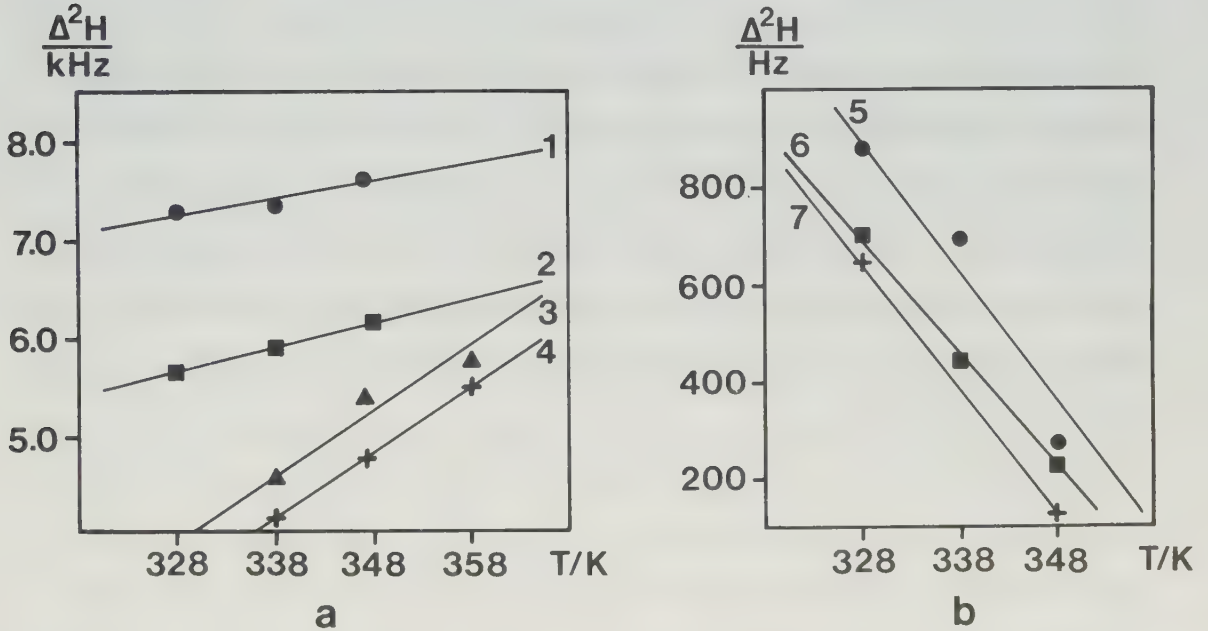


Fig. 7. A plot of Δ^2H as a function of temperature: 1) AD, 13.29 % w/w D_2O 2) AD, 17.57 % w/w D_2O 3) AS, 16.89 % w/w D_2O 4) AS, 19.78 % w/w D_2O 5) EDAS, 21.08 % w/w D_2O 6) EDAS, 25.68 % w/w D_2O 7) TAS, 22.48 % w/w D_2O .

DISCUSSION

PHASE DIAGRAMS AND DEUTERON NMR SPECTRA

When the inorganic counterion of an ionic amphiphile is replaced by a long-chained amphiphilic molecule the ability of the surfactant to form micellar solutions and thus even the solubility in water are dramatically reduced (1). Furthermore, in the binary catanionic surfactant - water systems the lamellar liquid crystalline phase seems to be favoured over other phase structures, such as hexagonal or cubic phases.

The extension of the lamellar mesophase of the catanionic systems as a function of temperature is also quite different from that of the systems that only contain the anionic or the cationic surfactant (1). Especially, the extension of the lamellar phases at higher temperatures seems to be reduced due to an appearance of an isotropic phase. The appearance of the isotropic phase as a function of temperature is discussed in detail elsewhere (14).

The Krafft temperatures in these systems are, as expected, higher than in octylammonium octanoate system (14), as hydrocarbon chains are longer. The interesting feature is that the Krafft temperatures decrease with the increasing size of the headgroup.

It is worth to take notice of the similarity of the AD and AS molecules: the strength of the hydration force, which is assumed to be the only repulsive interaction between the bilayers, seems to be the same in these systems. Also the deuteron splittings of the two systems are very

similar. The headgroups of these two molecules contain, besides the common ammonium ion, also a carboxylate ion and a sulphate ion, respectively. When alone, the end groups of carboxylate and sulphate ions show great differences both in the phase behaviour (1) and in the deuterium NMR spectra (70). But when the two molecules are incorporated in a lamellar aggregate, they have a very similar area per headgroup (67). Therefore, for the studied systems it seems that as far as the hydration force is concerned, it is not the chemical composition of the polar headgroups but rather the size of them that determines the strength of the repulsion.

The differences in the deuterium splittings in the AD and AS systems on one hand, and the TAS and EDAS systems on the other hand, can be explained by means of the exchangeable deuterons in the amphiphiles (71). The groups like $-\text{COOD}$ and $-\text{N}^+\text{D}_3$ will make the splittings larger, if the deuterium exchange is fast. In the TAS and EDAS systems no such groups are present and therefore the splittings of these systems are so much smaller.

ORIGIN OF THE REPULSIVE FORCE

As was mentioned above, it is of great importance that the electrostatic repulsion between the lamellar aggregates can be neglected. The conductivity measurements confirmed that the concentration of ionic surfactants, such as SDS, in the catanionic crystals is so low that it

cannot give rise to electrostatic effects.

We now consider the possibility that one of the ions A^+ or A^- has higher solubility in water than the other one, which could also result in a charged lamellar aggregate.

Assume a certain volume of the lamellar system, $V_{TOT} = A(L + b)$, where A is the area, and $2L$ and $2b$ are the thicknesses of the water layer and the hydrocarbon layer. The concentrations of the cations, c_+ , and anions, c_- , in water can be written as

$$c_+ = n_+/V = n_+/(N_A * A * L) \quad c_- = n_-/(N_A * A * L) \quad (9)$$

where n_+ and n_- are the number of cations and anions, respectively, in water, and N_A is the Avogadro's number. The surface charge density, σ , will then be the difference between the number of cations and anions in the lamellar aggregate

$$\sigma = -e * (n_+/A - n_-/A) = -e * N_A * L * (c_+ - c_-). \quad (10)$$

The maximum surface charge density is obtained if we assume that one of the components is totally insoluble in water, for example

$$c_+ \approx 0 \text{ and } n_+ \approx 0. \quad (11)$$

We can now calculate the concentration c_- , which would be required to reach a surface charge density $\sigma \approx 10^{-3} \text{ As/m}^2$. This is a very low value of σ , and the electrostatic repulsion between the bilayers with this surface charge density may be neglected compared with the dispersion force at the observed bilayer separations (14).

The concentration c_- can now be calculated from eq. (10)

$$c_- \approx 10 \text{ mM} . \quad (12)$$

The maximum solubility of A^- ions is now determined using a model from ref (2), where the chemical potentials for an amphiphile in a lamellar aggregate and in water, respectively, can be calculated.

In equilibrium, the chemical potentials of an A^- ion should be the same in the lamellar aggregate and in the water, the solubility of A^- ions can then be calculated from

$$\mu_{0l} + \gamma * A_A + kT \ln 1/2 = \mu_{0v} + kT \ln c_- \quad (13)$$

$$\mu_{0l} - \mu_{0v} + \gamma * A_A = kT * K(n_c)$$

where n_c is the number of carbon atoms in the hydrocarbon chain, and the parameter $K(n_c)$ can be found in ref. (69)

$$K (n_C) \approx -1.34 * n_C + 2.93 \quad (14)$$

The concentration c_- then becomes

$$c_- = 1/2 * \exp[K(n_C)] , \quad (15)$$

and for $n_C = 12$

$$c_- \approx 10^{-3} \text{ mM} . \quad (16)$$

Compared with the eq. (12) , this means that the solubility of A^- in water is about 10000 times lower than what would be required to obtain a surface charge density $\sigma \approx 10^{-3} \text{ As/m}^2$ in the lamellar aggregate. Consequently, the repulsion between the bilayers cannot be due to the differences in the solubilities of A^+ and A^- .

However, it is important to notice that this may not be true in all kinds of systems where a cationic and an anionic surfactant are mixed with water. The catanionic systems that are studied in this work are quite special. Firstly, the hydrocarbon chains are long enough, $n_C = 12$. As can be calculated from the eq. (15) , the chain lengths should not be shorter than $n_C = 8$, to assure that the electrostatic effects can be neglected. Secondly, both the anionic and the cationic surfactants have the same hydrocarbon chain length and thus approximately the same solubility in

water. Moreover, maximal water layer thickness is less than 15 Å in these systems.

We can see from the eqs (10) and (15) that the surface charge density is a function of both the hydrocarbon chain length, n_C , and the thickness of the water layer, L . If we let the chain length of the cationic surfactant be a constant, $n_{C+} = 12$, and vary the chain length of the anionic surfactant, n_{C-} , we can calculate σ for different values of n_{C-} from eqs (10) and (15).

In Fig. 8, $\log \sigma$ is plotted as a function of n_{C-} , the solid line is obtained when $L = 7$ Å and the dashed line when $L = 200$ Å.

The Fig. 8 shows that σ increases rapidly when $n_{C-} < n_{C+}$, but when $n_{C+} < n_{C-}$ the σ reaches soon a constant value. For $L = 200$ Å, this effect is even more drastic.

We can conclude that as far as we want to have a system where the electrostatic effects can be neglected, it is a great advantage that the two hydrocarbon chains in a catanionic molecule have the same length. Especially, if the lamellar phase can swell up to very high water contents, only small differences in the hydrocarbon chain lengths may have considerable effects on the surface charge density.

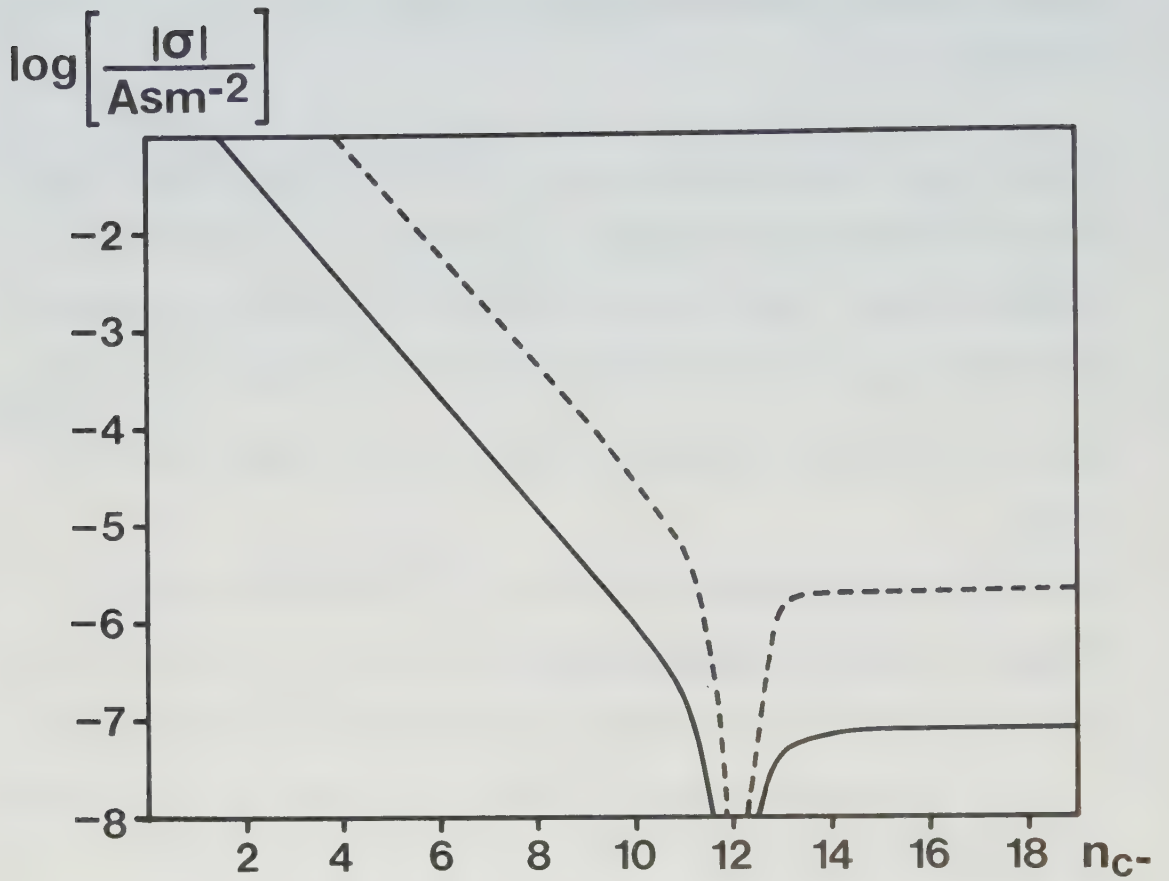


Fig. 8. A plot of $\log \sigma$ versus the hydrocarbon chain length of the anionic surfactant, n_{C^-} , when the chain length of the cationic surfactant, $n_{C^+} = 12$. The solid line is for $L = 7 \text{ \AA}$ and the dashed line for $L = 200 \text{ \AA}$.

HYDRATION FORCE AND HYDROPHOBIC INTERACTION

It seems that the DLVO theory is not sufficient to describe the behaviour of certain kinds of colloidal systems, especially when two hydrophilic or hydrophobic surfaces are separated by an aqueous layer. In the former case there exists an additional repulsive force in addition to the van der Waals attraction and the electrical double layer repulsion. This force is usually called hydration force (23 -41, 76 - 86, 89), or sometimes also "structural component of disjoining pressure" (73). In the latter case, the additional force is attractive and it is called the hydrophobic interaction (42 - 48).

HYDRATION FORCE

The hydration force has been verified between rigid, molecularly smooth surfaces and, also between fluid and more rough surfaces. The hard surfaces can be of various types: surfaces of glass (72, 73), metals (74) and silica (74) in aqueous solutions have been studied, as well as the swelling of the clays (75). In a series of papers, Pashley and Israelachvili have measured forces as a function of separation between two mica surfaces immersed in aqueous solutions (76 - 83).

The same technique has been used in the systems where either quaternary ammonium salts are adsorbed directly on mica (84) or bilayers of cationic amphiphiles (85), phospholipids (31, 32) or galactolipids (86) are adsorbed on a mica surface.

On the other hand, also forces across soap films (87, 88) and forces between parallel DNA-double helices (89) have been measured. Parsegian and coworkers have in a series of papers studied phospholipid bilayers in water (23 - 30). They have measured directly the force versus the distance between the bilayers, and have also studied the effect of charged phospholipids (25) and added divalent cations (27, 28).

According to the experimental information, the hydration force is assumed to be a strong, exponentially decaying repulsive force with the decay length of 0.2 - 0.3 nm for lipid bilayers and 1 nm for hard surfaces. The force can be described by the empirical equation:

$$P_{HF} = P_0 * \exp(-d/\lambda) \quad (17)$$

where P and d are the pressure and the distance between the surfaces, and λ and P_0 are constants, that are specific for each system.

In fact, the hydration force can be considered as a special case of solvation forces between two surfaces separated by a liquid medium. In non-aqueous medium there is an oscillating force operating between two surfaces (90 -98). An oscillating force can also be found at very small separations (<1.5 nm) between two rigid surfaces in an aqueous medium (99). In this kind of systems, the oscillating component is, however, superimposed on a long-range monotonic component. No oscillating component is found in bilayer systems, probably because the oscillations are smeared out by fluctuations in the bilayers.

Although there is a lot of experimental information on the hydration force interactions between different kinds of hydrophilic surfaces, the theoretical understanding of the force is still limited. Several different theories are suggested in order to describe the molecular origin of the hydration force.

Helfrich has proposed a model for fluid, fluctuating membranes (33). In his model, the repulsive hydration force is a result of the steric interactions of the membranes in multilayer systems. When two bilayers of fluid membranes approach each other the amplitude of the fluctuations decreases and this gives rise to an excluded volume contribution to the free energy. This effect will then result in a repulsive force between the bilayers. The repulsive force is of the same order of magnitude as the van der Waals attraction; at small bilayer separations the attractive force is stronger than the repulsive force, while at large separations the repulsive force dominates.

According to the theory of Marcelja, Gruen and coworkers the hydration force is a result of a perturbation in the water structure (34 - 37). The water in the model assumed to possess an ice-like structure with a large concentration of bonding defects. Interaction between two parallel, planar surfaces is determined by separate spatial variations of the electric and the polarization fields in the aqueous layer between the plates. Near the surface, the interaction is dominated by the polarization field and this induces an orientation of water molecules lying next to the

surface. At short range, the coupling between the electric and the polarization fields results in a strong, exponentially decaying repulsive force between the surfaces. At longer range, the interaction can be described as a double-layer repulsion between two plates with an effective surface charge.

Kjellander and Marcelja have used molecular dynamics simulations for calculations of water structure between mica sheets and lecithin bilayers (38, 39). The surfaces are considered as rigid lattices of atoms. The discrete surface charges give rise to an electrostatic field, which will change the water orientation near the surface. This orientation leads to unfavourable changes in hydrogen bonding between the water molecules, and if two surfaces approach each other this interaction results in a repulsive hydration force.

Quite a different theoretical model was suggested by Jönsson and Wennerström (40, 41). In this model, both water and the hydrocarbon layers are treated as continuous media, and the hydration force is due to the dielectric discontinuities at the water-hydrocarbon interfaces. When a polar molecule is fixed at a bilayer surface it will induce polarization charges at the interfaces. The same interaction can also be obtained by using the so called image forces.

There are two contributions to the image electrostatic interactions (41): The first one, which is repulsive and dominates at short separations, appears because the water is replaced by hydrocarbon in the outer solvation region for the polar headgroups. The second contribution, which

is attractive and dominates at long range, is due to the direct interactions between the headgroups of opposite lamellae.

Our experimental results show that the hydration force between the bilayers increases with increasing size of the headgroup. However, when the ammonium ion is replaced by the trimethylammonium ion and further by ethyldimethylammonium ion the polar headgroup also becomes more hydrophobic.

Even if the theory of Helfrich may not be able to give correct quantitative results for the hydration force interactions, it could be applied qualitatively on the catanionic bilayers. When the polar headgroups become larger it may become easier for the lamellae to fluctuate and therefore, the repulsive force should increase with increasing size of the headgroups.

According to the theory, that is based on the water structure, the behaviour of the catanionic systems should be totally different: Hydrophobic headgroups are not able to polarize the water molecules and the hydration force is therefore expected to decrease with increasing hydrophobicity of the headgroups.

The continuum model may, however, explain the experimental results. According to this theory, the distance where the attractive and the repulsive forces balance depends on the polarizability of the charged layer. The polarizability is represented by a parameter Δ which is the distance

between the dielectric discontinuity and the charged layer; when the size of the headgroup is increased, the parameter Δ will also increase (41). The results (41) of the calculation of the osmotic pressure as a function of the distance between the bilayers for some different values of Δ are shown in Fig. 9. In Fig. 9a, the negative and the positive layers at the surface are separated by a certain finite distance which is assumed to be the case for zwitterionic bilayers. In Fig. 9b, the two charges are lying in the same plane, and this model can be applied on the catanionic systems. In agreement with the experimental results, the diagrams show that when the values of Δ are increased, the repulsive pressure will operate at longer distances, i.e. when the polar headgroups become larger the lamellae can swell more.

It is also interesting to compare the proposed swelling for the same Δ - values in Fig. 9a and 9b, respectively. According to the model, the zwitterionic lamellae should swell more than the corresponding catanionic lamellae with the same size of the headgroup molecules. The experimental results for the aqueous systems containing lecithin and phosphatidyl-ethanolamine, respectively, show, indeed, that the maximum thickness of the water layer is roughly twice the values that were calculated from the eq. (7) for the TAS and AS systems (15, 21, 22, 30).

However, the comparison of zwitterionic and catanionic systems can not be done straightforwardly. From the X-ray diffraction measurements the total thickness of the water layer is obtained, but the measurements do not give any information of the polar layer, which is occupied by the amphiphilic headgroups. However, especially in the zwitterionic lamellar systems, the headgroups are so large and bulky that the thickness of the

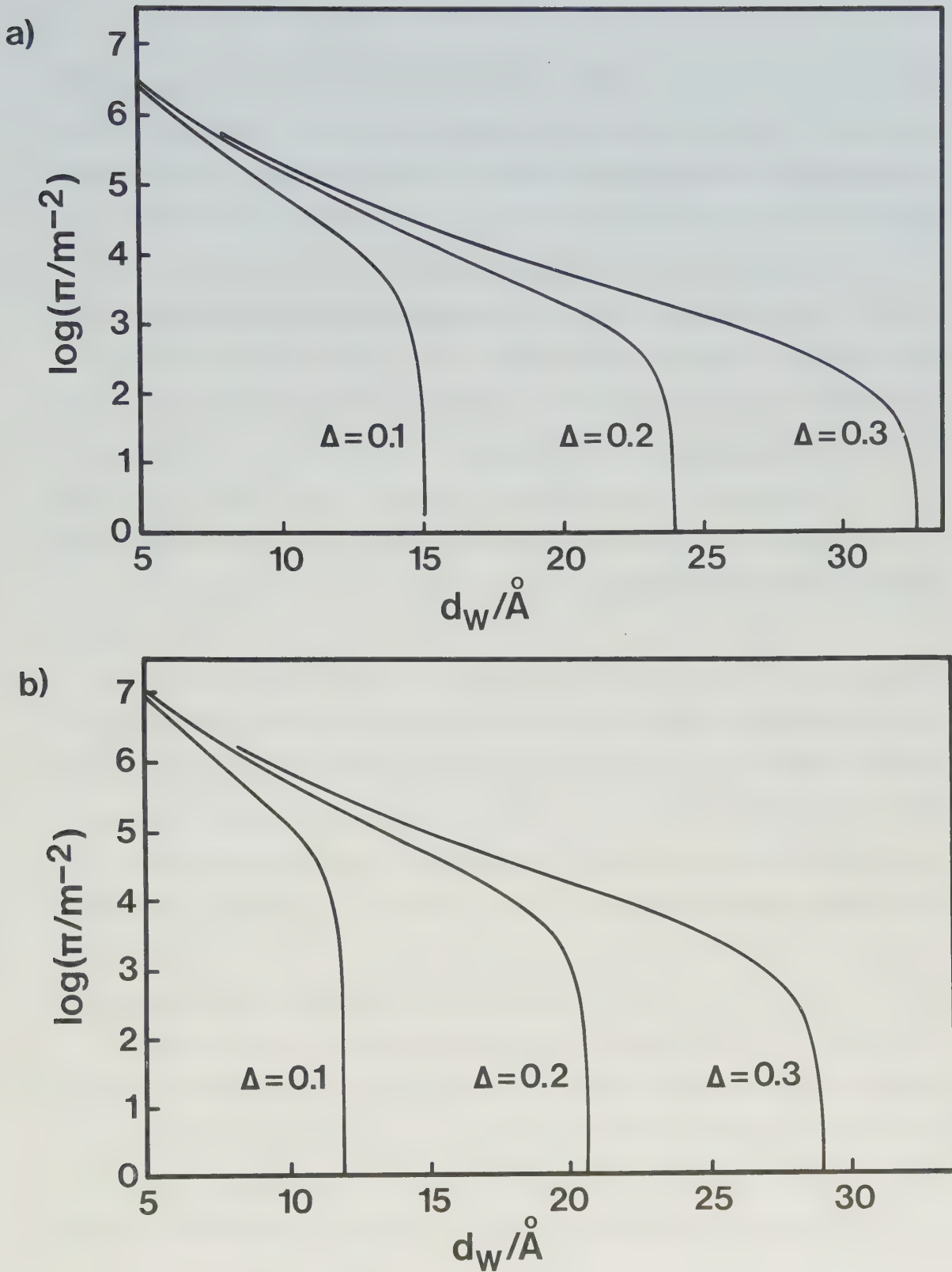


Fig. 9. Calculated osmotic pressure Π_0 , from the ref. 41, for three different Δ -values. a) A system where the positive and negative charges of a zwitterion are separated by a certain distance. b) A system with both positive and negative charges in the same plane.

polar layer should be taken into account when the bilayer separations are calculated. The problem is that the zwitterionic headgroups are not fixed in well-defined positions relative to the hydrocarbon surface, but they are able to fluctuate relatively freely. Therefore, it is only possible to obtain a rough estimation of the polar layer thickness.

In the lamellar phase of a catanionic surfactant - water system where both headgroups are lying approximately at the same distance from the hydrocarbon surface, the polar layer thickness should be considerably smaller than in the zwitterionic systems.

HYDROPHOBIC INTERACTION

In the studied catanionic systems, we assume that the two dominating forces are the van der Waals attraction and the hydration force repulsion. In some systems where two hydrophobic surfaces are separated by a water layer, another strong attraction, in addition to the van der Waals force, is observed between the surfaces. This attraction is usually called hydrophobic interaction.

Forces between monolayers of some long-chained amphiphilic substances adsorbed on mica surfaces have been measured as a function of the distance between the surfaces (42, 46 - 48). The experimental results show that below a distance of 10 nm there is a strong, apparently exponentially decaying attraction with a decay length of of 1.0 - 1.4 nm operating between the hydrophobic surfaces. The strength and the range of

this attraction depend on the hydrophobicity of the surface, but the force is strong relative to the conventional van der Waals forces.

Similar results have been obtained when forces between hydrophobized glass and quartz filaments have been measured (43).

The molecular origin of the hydrophobic interaction is not clear, even though some theories have been suggested.

One of the models is based on the surface induced perturbations in the water structure (48). Due to the incapability of the hydrophobic molecules to form H-bonds, water molecules orient in an entropically unfavourable way in the vicinity of a hydrophobic surface. The total free energy of the system will decrease when the water molecules are pressed from the water layer between the surfaces into the bulk solution.

Another theory does not involve any specific hydrophobic force between the surfaces (43 - 45). For strongly hydrophobic surfaces, the water - surface interface has a higher energy than the interface between the water vapor and the surface. Therefore, if two hydrophobic surfaces separated by a water layer approach each other, a cavity filled with water vapor may form between them, if a certain energy barrier can be overcome. In one of the experiments, some evidence for cavitation was found (47).

Our experimental results do not show any increasing effect of the hydrophobic interaction when the polar headgroups are made more hydrophobic. One reason may be that even the largest headgroup used, containing an ethyldimethylammonium ion, is still quite small compared

with the long-chained amphiphilic molecules which are studied earlier. On the other hand, also the presence of less hydrophobic sulphate groups may have an effect on the interactions between the lamellar aggregates. Apparently, the hydrophobic interactions can only be observed if two very strongly hydrophobic surfaces are separated by a water layer.

SUMMARY

In this work, we have studied the effect of replacing the inorganic counterion of an ionic surfactant with an oppositely charged long amphiphilic ion and, what is more, all possible inorganic counterions are eliminated from the system. As the two surfactants have approximately the same solubility in water the electrostatic effects can be neglected in the binary catanionic surfactant - water systems.

The experimental phase diagrams for catanionic surfactant -water systems show that above 373 K, the lamellar phase is replaced by an isotropic phase where the bulk phase consists of melted surfactant. Below this temperature, the phase-equilibria of the catanionic systems resemble the phase equilibria of a lecithin - water system, showing a lamellar phase in equilibrium with almost pure water.

As the lamellar aggregates are uncharged, the swelling of the lamellar phase is assumed to be due to the hydration force interactions between the bilayers. It seems that the strength of the hydration force is more dependent of the size of the polar headgroups than the specific chemical

composition of them. Furthermore, no hydrophobic attraction could be observed between the bilayers.

Therefore, the interactions between the lamellae are better described by the theory that treats water as a continuous medium than the model which is based on the surface induced changes in the water structure.

Due to the structure of the polar headgroup, the lamellar phase of catanionic systems should be more suitable for theoretical model studies of hydration force than the lamellar phase of a zwitterionic phospholipid systems. The regular polar surface of a lamellar aggregate created by A^+A^- -molecules could even be used as a model system for a two-dimensional ionic lattice.

The aqueous systems which contain both an anionic and a cationic surfactant have thus shown many interesting new properties, and this kind of systems may also have practical applications. The study of a ternary system catanionic surfactant - water - a long-chained alcohol is under investigation at our laboratory.

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511.



**Phase equilibria of
catanionic surfactant -dodecanol - water
systems**

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ABSTRACT

In this work, the phase equilibria in two ternary systems containing a catanionic surfactant, dodecanol and water are studied. The studied catanionic surfactants are dodecylammonium dodecanoate (AD) and dodecyltrimethylammonium dodecylsulphate (TAS).

The experimental phase diagrams show that adding an uncharged amphiphilic molecule to the binary catanionic surfactant - water systems leads to an increasing uptake of water in the lamellar phase. As the lamellar aggregates in the studied systems are uncharged, the increasing swelling of the lamellar phase is due to an increased repulsive hydration force between the lamellar bilayers. This observation is discussed in light of an electrostatic theory which is suggested for the hydration force interaction (Jönsson, B. and Wennerström, H., *Chemica Scripta* 25, 117, 1985).

At higher dodecanol concentrations a reversed hexagonal phase begins to form and at still higher alcohol concentrations a reversed micellar phase appears.

In the TAS system, where the melting point of the surfactant crystals is relatively high, the lamellar phase becomes more stable relative to the crystals with increasing temperature, in the temperature range 308 - 333 K. The eutectic melting point of the surfactant crystals in the AD system is lower, and on melting an isotropic phase is formed. In this system, increasing temperature favours the isotropic phase.

INTRODUCTION

In the previous studies (1, 2), we have seen that catanionic systems, which contain both a cationic and an anionic surfactant, possess many interesting properties which are quite different from those of systems where only the cationic or the anionic surfactant is present. We have studied binary systems containing a catanionic amphiphile and water (2), and also a ternary system of octylammonium octanoate - sodium octanoate - water (1). The experimental results showed that at ambient temperatures, the binary systems of a catanionic amphiphile and water are very similar to lecithin - water systems where the only liquid crystalline phase, the lamellar phase, is in equilibrium with almost pure water. As the lamellar aggregates are uncharged in these systems, it was assumed that the dominating forces between the bilayers are the attractive van der Waals force and the repulsive hydration force. According to the experimental results, it seems that the hydration force in the studied systems is more dependent on the size of the polar headgroup than its specific chemical composition (2).

On the other hand, the phase equilibria of the octylammonium octanoate - sodium octanoate - water system show that only very small amounts of an ionic amphiphile are required to make the electrostatic repulsion between the lamellae dominate over the van der Waals interaction. Consequently, the addition of an ionic component leads to a drastic increase in the swelling of the lamellar phase (1).

The aim of the present work is to investigate how the hydration force repulsion in the lamellar phase of the catanionic systems is effected by an addition of uncharged amphiphile, in this case a long-chained alcohol.

Therefore, we have studied phase equilibria of two different three component systems consisting of a catanionic surfactant, dodecanol and water. The catanionic surfactants used are dodecylammonium dodecanoate (AD) and dodecyltrimethylammonium dodecylsulphate (TAS).

These surfactants are chosen because the studies of the binary systems of catanionic amphiphile - water showed that as the latter surfactant has a larger and bulkier head group than the former one, there is a considerable difference in the strength of the repulsive hydration force in the two systems.

The experimental results are also discussed in the light of an electrostatic theory (3,4) which is suggested in order to explain the molecular origin of the hydration force.

MATERIALS AND THE SAMPLE PREPARATION

The preparation of the catanionic surfactants, TAS and AD, is described previously (2). Dodecanol (99 %) was obtained from BDH, England and the heavy water (99.7 %) from Merck, Germany, and they were used without further purification.

The samples consist of three components: one of the two catanionic surfactants, dodecanol and heavy water, and they were prepared by weighing the components directly in glass ampoules which were flame sealed. The samples were mixed by warming to 323 K and repeated

centrifugation. After that they were equilibrated at 323 K at least one week before the first NMR measurement was made. The samples were mixed and equilibrated once more, and after this the second NMR measurement was carried out. No significant difference between the first and the second NMR measurements was observed. After the thermodynamic equilibrium was achieved, the samples were stored at room temperature.

METHODS

The samples were first examined against crossed polaroids in order to ascertain the homogeneity and the occurrence of birefringency. The samples that contain anisotropic phases were further examined by deuteron NMR technique and polarizing microscopy.

^2H NMR study was made at a resonance frequency of 39.14 MHz on a home-built Fourier transform spectrometer equipped with an Oxford Instrument 6-T wide-bore superconducting magnet.

The deuteron NMR spectra were recorded at 333 K. The analysis of spectra as well as the operation of the spectrometer were described previously (2).

The polarizing microscopy studies were used as a complementary method, in order to check the structure of the liquid crystalline phases. The lamellar phase structure was identified by a mosaic texture, whereas the

hexagonal structure showed a non-geometric striated texture in the microscope (5). The existence of crystals was also easily confirmed.

The two-phase samples that contain two isotropic phases ($L_2 + W$), were used to estimate the phase boundary of the L_2 -phase. For this purpose, we assume that the L_2 -phase is in equilibrium with pure water. The volume of the water phase in a two-phase sample is measured, and since the density of the heavy water is known the weight of the water phase can be obtained from a calibration diagram. From the total weights of the three components the weight fraction of water in the L_2 -phase can easily be calculated. In this way, we obtain the tie-lines between the water corner and the L_2 -phase, shown in Figs 1 and 5.

RESULTS

TAS - DODECANOL - WATER SYSTEM

An approximative phase diagram of TAS - dodecanol - water at 333 K is shown in Fig. 1. The symbols used to denote different phase structures are based on the Ekwall's system (9, 13). Besides the crystalline surfactant, the phase diagram contains four one- phase regions: Two isotropic phases (W and L_2) and two anisotropic phases (D and F). The structure of the lamellar phase, D , is easily confirmed in the polarizing microscope.

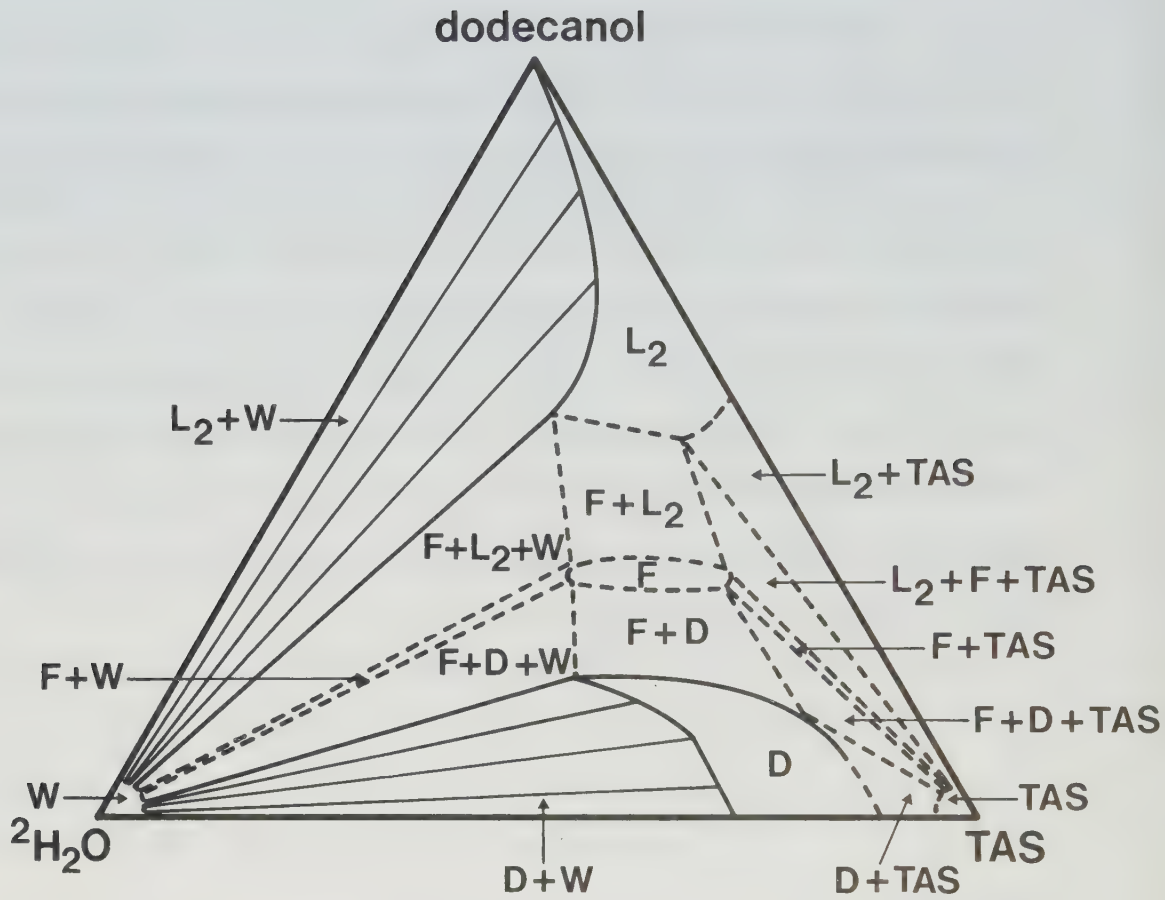


Fig. 1. Approximative phase diagram for the system TAS - dodecanol - water at 333 K. The homogeneous one-phase regions are denoted by:

D = lamellar mesophase

W = isotropic solution, almost pure water

L_2 = isotropic solution, reversed micelles

F = reversed hexagonal mesophase

TAS = TAS crystals

In order to determine the structure of the three other one-phase regions, we have also to consider their location in the phase diagram relative to the other phases (5 - 22).

The lamellar mesophase consists of the surfactant bilayers alternating with water layers as shown in Fig. 2. In the studied systems, the solubilities of the amphiphilic molecules in water are assumed to be so low that both the catanionic surfactant and the alcohol molecules are incorporated in the bilayers.

As the solubility of TAS in water is very low, we assume that the isotropic phase at the water corner of the diagram, W, consists of almost pure water. Furthermore, the bulk of the other isotropic solution, L_2 , is assumed to consist dodecanol which is able to dissolve some water when catanionic surfactant is added to the system. This is possible if the surfactant molecules form reversed micellar aggregates with their hydrocarbon chains in contact with the dodecanol solution. Water can then be solubilized in the hydrophilic interior of the reversed micelles, as shown in Fig. 3a.

The liquid crystalline phase which is situated between the lamellar phase and the L_2 -phase shows a hexagonal texture in the polarizing microscope.

The hexagonal phase is composed of long cylindrical aggregates which are packed in a hexagonal array, as shown in Fig. 3b. In the studied systems, the water content of the hexagonal phase is so low that the phase is assumed to possess a reversed hexagonal structure, F, where the hydrocarbon chains of the catanionic surfactant and the alcohol molecules occupy the space between the hexagonally packed water cylinders. The precise boundaries of this phase were not determined.

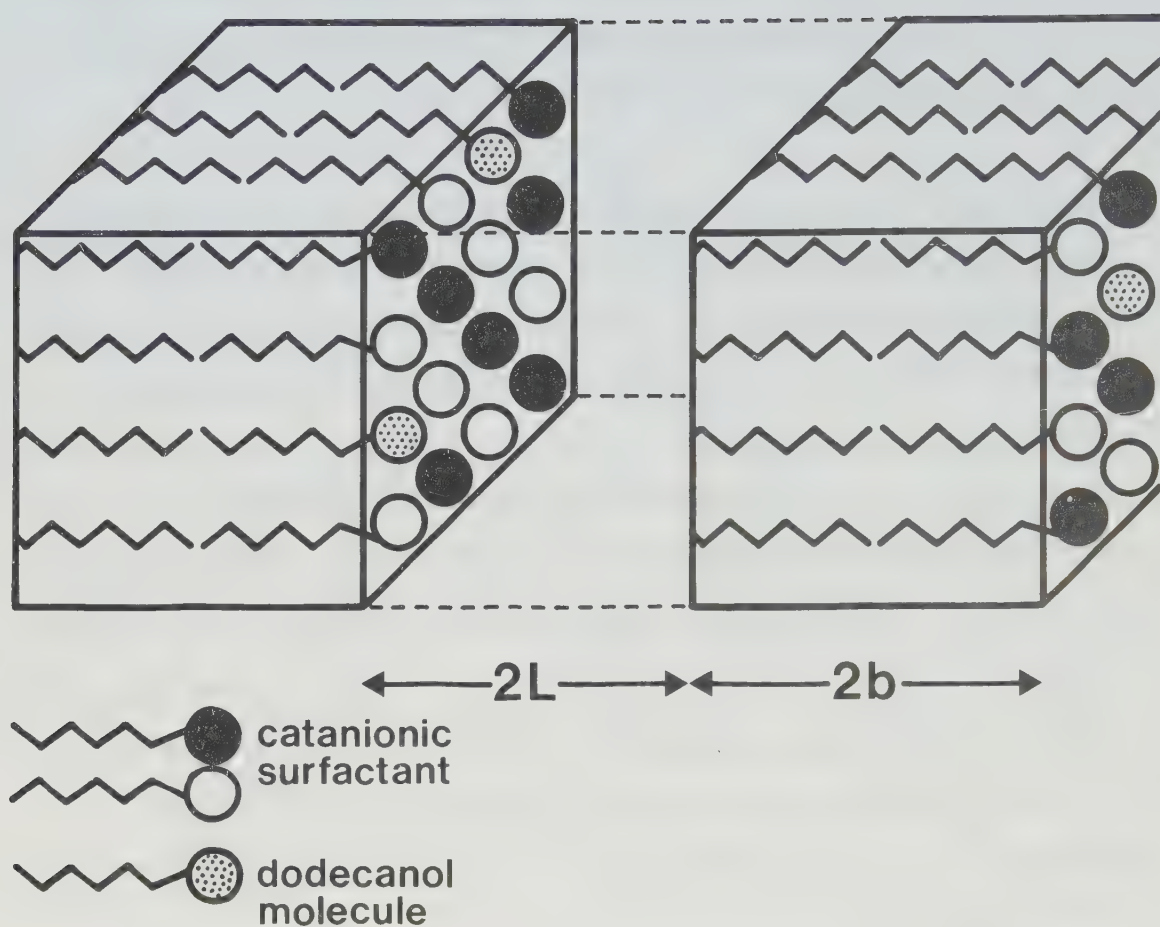


Fig. 2. Schematic representation of a lamellar system, containing a catanionic surfactant, dodecanol and water. The thickness of the amphiphilic bilayer is $2 \times b$, and the thickness of the water layer is $2 \times L$.

The most important feature in the phase diagram is the extension of the lamellar phase, which at 333 K is in equilibrium with the W-phase, the F-phase and the TAS crystals.

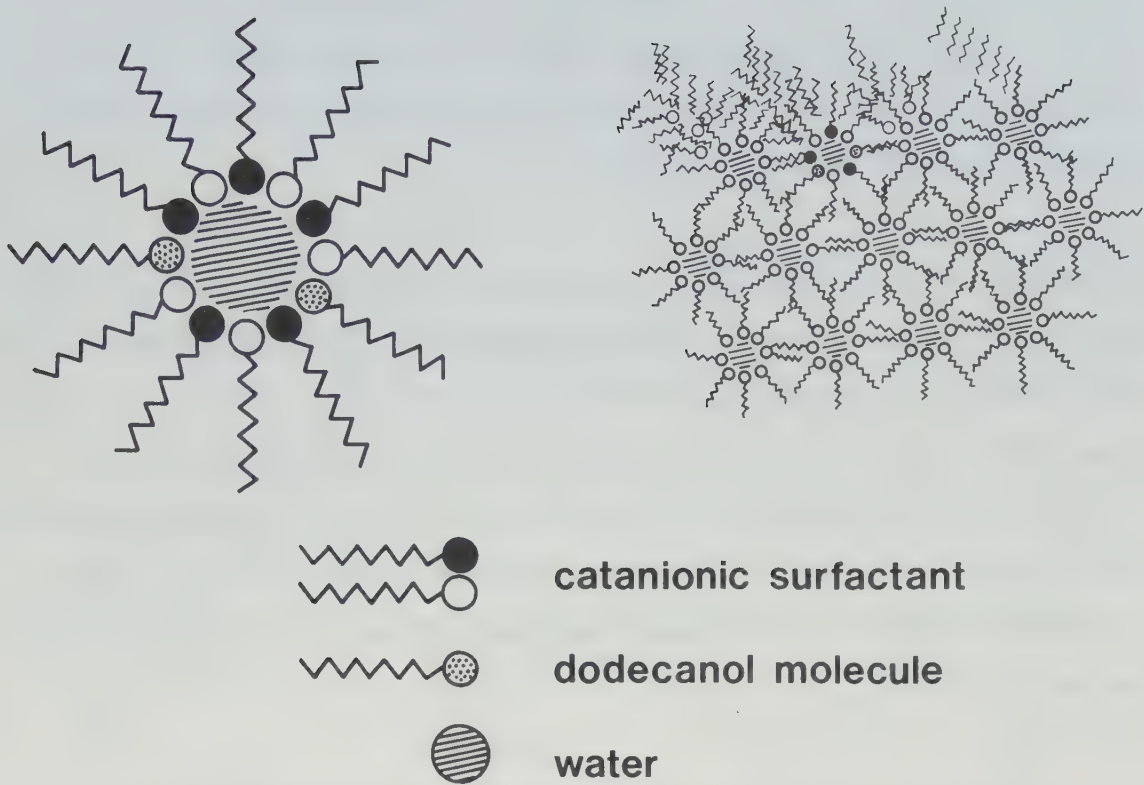


Fig. 3. Schematic representation of a) a reversed micellar system, and b) a reversed hexagonal system. See text for further explanation.

The maximum uptake of water is 30 % w/w in the lamellar phase of the binary system TAS - water (2). When dodecanol is added to the system the swelling of the lamellar phase increases first slightly, but after an addition of 10 % w/w alcohol this trend becomes more drastic. The maximum uptake of water, 37 % w/w, is reached after addition of 16 % w/w dodecanol.

The polarizing microscopy studies show that the Krafft temperature of the lamellar phase is 308 K, and that this phase structure is stable up to 383 K; above this temperature the samples become isotropic. In the temperature range 308 - 383 K, the temperature has only a small effect on the swelling of the lamellar phase (2).

Above the concentration of 16 % w/w dodecanol, the lamellar phase is in equilibrium with the reversed hexagonal phase, F. The balance between the two phases is, however, dependent of the temperature: In the temperature range 308 - 318 K, the lamellar phase seems to be able to incorporate more than 16 % w/w dodecanol, but above 318 K, when the hexagonal phase first occurs, the F-phase begins to suppress the lamellar phase. On the other hand, the hexagonal phase disappears and an isotropic phase forms already at 373 K.

The extension of the lamellar phase towards the waterpoor part of the phase diagram is reduced by the occurrence of TAS crystals. Also in this case, the balance between the two phases depends on temperature; the lamellar phase becomes more stable relative to the crystalline phase with increasing temperature. In Fig. 4, the extension of the D-phase towards the TAS corner is shown at some different temperatures. The temperature dependence of the phase boundary between the D-phase and the two-phase region D+F is not shown in the figure.

As the D-phase, the L_2 -phase is at 333 K in equilibrium with the W-phase, the F-phase and the TAS-crystals. As was mentioned above, the continuous medium of the L_2 -phase is assumed to be dodecanol.

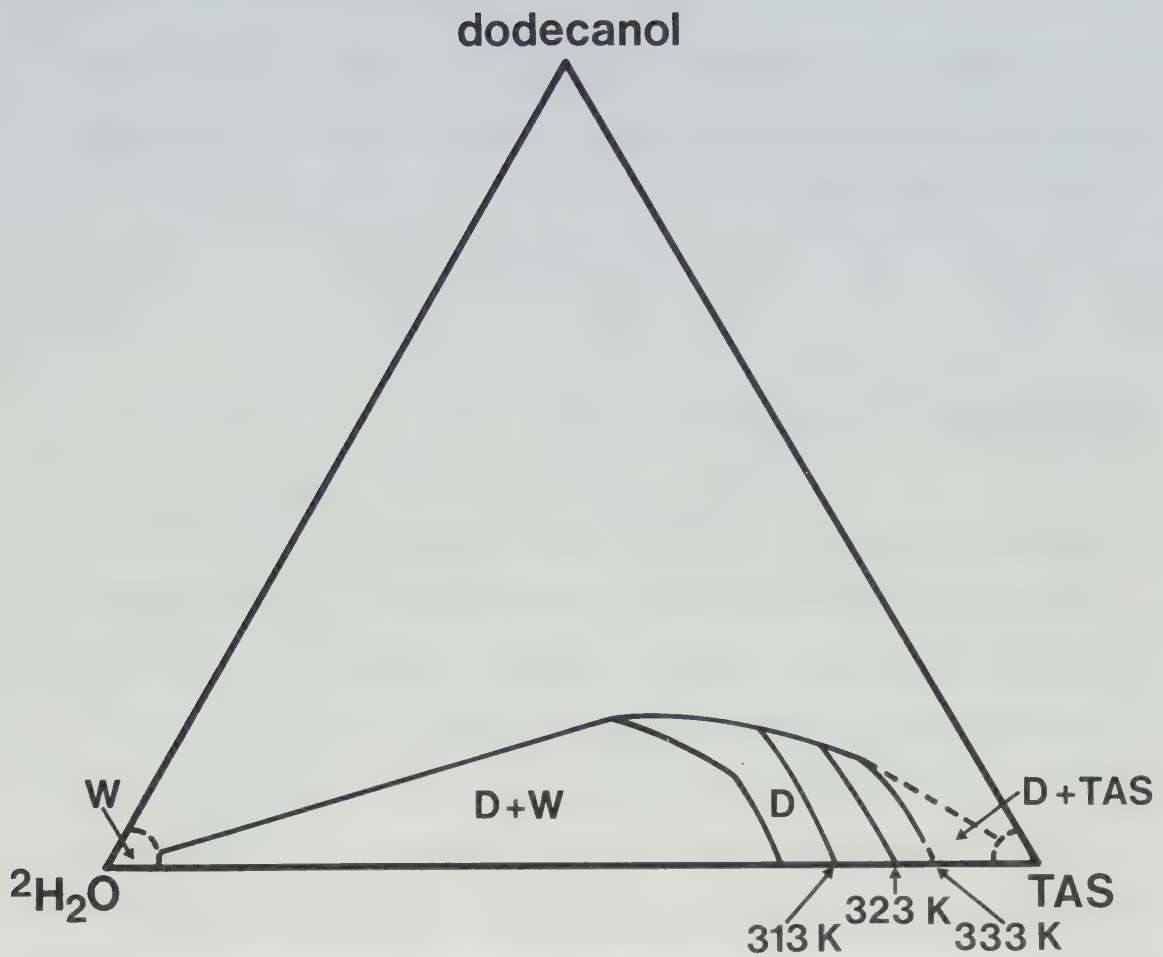


Fig. 4. A partial phase diagram of the system TAS - dodecanol - water, showing the extension of the lamellar phase, D, at some different temperatures.

The phase diagram shows that pure water and pure dodecanol are practically insoluble in each other, but when surfactant is added to the system dodecanol is able to solubilize up to 20 % w/w water.

The boundaries between the L_2 -phase and the two-phase regions $F + L_2$ and $G + L_2$, respectively, are dependent on the temperature. The L_2 -phase becomes more stable relative to the F-phase and the TAS crystals with increasing temperature.

AD - DODECANOL -WATER SYSTEM

An approximative phase diagram of AD - dodecanol - water at 333 K is shown in Fig. 5. Besides the phase of AD crystals, the phase diagram contains five one-phase regions: three isotropic phases (W , L_2 and AD_m) and two anisotropic phases (D and F). The structure of the different phases was determined in the same way as in the TAS - dodecanol - water system. The W -phase consists of almost pure water, while the L_2 -phase has dodecanol as the continuous medium.

AD_m denotes a reversed micellar phase where the water is incorporated in the polar interior of the aggregates, as shown in Fig. 3a. But in contrast to the L_2 -phase, the continuous medium of the AD_m phase is assumed to consist of melted surfactant which can dissolve some dodecanol. The addition of dodecanol to the AD crystals seems to lower the eutectic melting point, so that the AD_m -phase extends from higher dodecanol concentrations to lower ones with increasing temperature.

As no detailed studies were made in this isotropic region, it is not known if the two phases, L_2 and AD_m , exist as two separate phases. The hatched

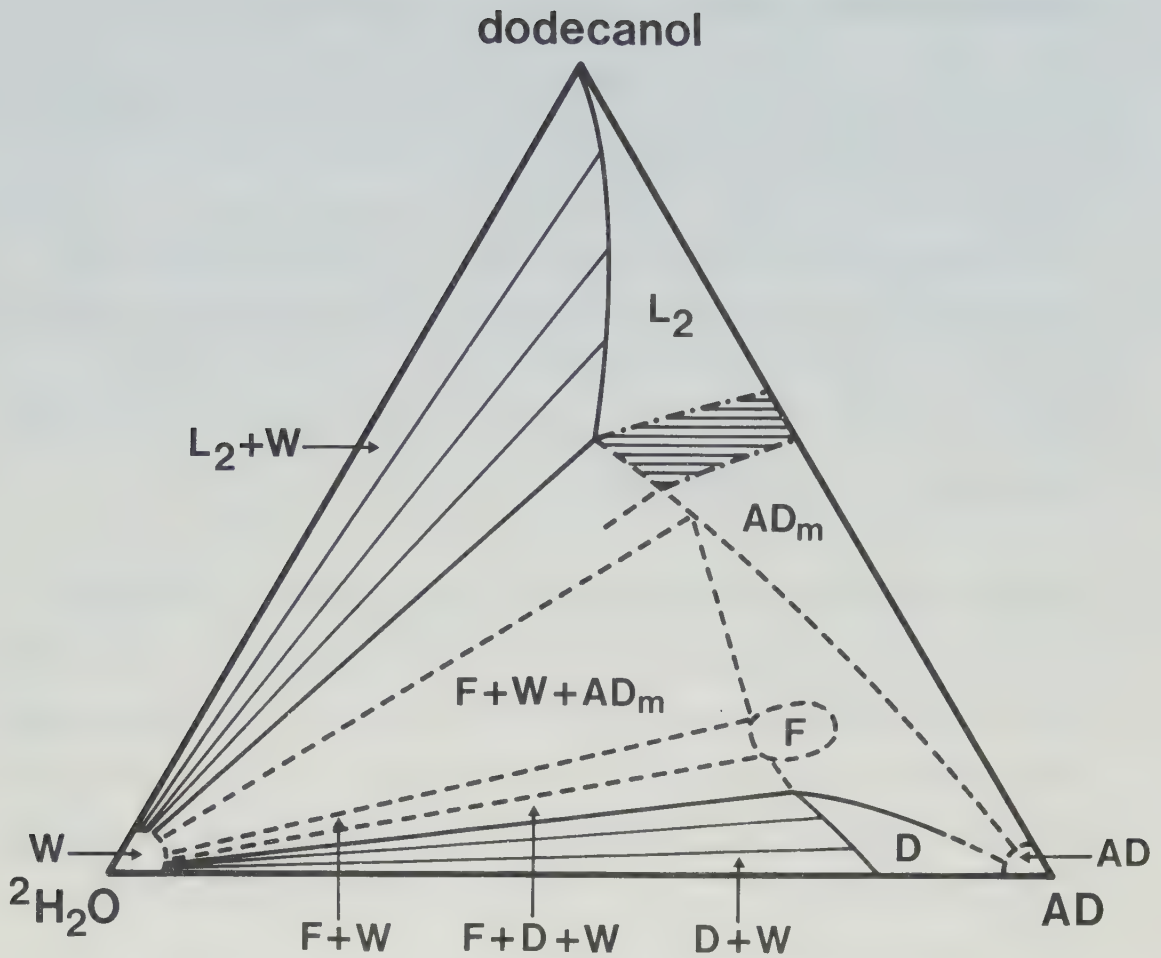


Fig. 5. Approximative phase diagram for the system AD - dodecanol - water at 333 K. The homogeneous one-phase regions are denoted by:

D = lamellar mesophase

W = isotropic solution, almost pure water

L_2 , AD_m = isotropic solution, reversed micelles

F = reversed hexagonal mesophase

AD = AD crystals

region in the phase diagram shows the approximate location of the possible two-phase region.

The lamellar phase of this system may at 333 K be in equilibrium with the W-phase, the F-phase and the AD_m -phase.

The maximum uptake of water is 19 % w/w in the lamellar phase of the binary system AD - water (2). When dodecanol is added to the system the swelling increases, but not as drastically as in the system of TAS - dodecanol - water. The maximum uptake of water, 22 % w/w, is reached after addition of 10 % w/w dodecanol.

Above this dodecanol concentration, the lamellar phase is in equilibrium with the reversed hexagonal phase, F. The precise location of the F-phase was not determined, but also in this system the balance between the two phases seems to be dependent of the temperature: Immediately above the Krafft temperature, 318 K, the lamellar phase may be able to incorporate more dodecanol than 10 % w/w; when the F-phase occurs at 323 K it begins to suppress the lamellar phase.

The extension of the lamellar phase towards the waterpoor part of the phase diagram is effectively reduced by the occurrence of the isotropic AD_m -phase. As the temperature is above the eutectic melting point of the AD - water system (2) the lamellar phase decreases rapidly with increasing temperature. At higher dodecanol concentrations, the lamellar phase is replaced by the isotropic phase already at 338 - 343 K, and from the binary phase diagram of AD - water (2), we know that the lamellar phase has totally disappeared at 358 K.

The L_2 -phase in the ternary TAS - dodecanol - water system is at 333 K in equilibrium with the two other isotropic phases, W and AD_m . Although the maximum amount of water that can be solubilized in dodecanol when AD is added to the system is the same as in the TAS - dodecanol -water system, 20 % w/w, it seems that for the same amount of the added catanionic surfactant, dodecanol is able to dissolve more water in the AD - dodecanol - water system.

DISCUSSION

The most important feature in the two studied phase diagrams is the observed increasing uptake of water in the lamellar phase when dodecanol is added to the binary catanionic surfactant - water systems.

It is also interesting to notice, that above the dodecanol concentrations where the alcohol can be incorporated in the lamellar phase, further addition of dodecanol to the systems favours the formation of reversed phase structures.

On the other hand, there is also some important differences between the two phase diagrams. The extension of the lamellar phase in the AD system is strongly reduced compared with the TAS system, and the isotropic phase which has melted surfactant as the continuous medium is only

present in the AD system.

HYDRATION FORCE REPULSION

As the lamellar aggregates are uncharged in the binary systems of catanionic surfactant - water, the swelling of the lamellar phase in these systems is assumed to depend on the balance between the attractive van der Waals force and the repulsive hydration force (2). In these systems, the strength of the hydration force seems to be more dependent on the size of the polar headgroup than its specific chemical composition. On the other hand, as the hydration force repulsion has relatively short range, the maximum uptake of water in the lamellar phase of these systems is in the range 19 - 35 % w/w.

Addition of a charged amphiphile to a binary system catanionic amphiphile - water, gives rise to an electrostatic repulsion between the bilayers. As the electrostatic repulsion operates at longer distances than the hydration force, lamellar phases with charged aggregates are able to swell much more than those with uncharged ones. The experimental phase diagram of the ternary system octylammonium octanoate - sodium octanoate - water showed that an addition of 3 % w/w sodium octanoate to the binary system octyl- ammonium octanoate - water made the lamellar phase swell from a water content of 25 % w/w to 80 % w/w. Theoretical calculations of the phase equilibria in the same system predicted that the electrostatic double layer repulsion begins to dominate over the van der Waals interactions already if the lamellar aggregate contains 1 % w/w charged amphiphile.

When an uncharged amphiphile is added to a binary catanionic surfactant - water system, there will not be any electrostatic repulsion, but the dominating forces between the bilayers are still the van der Waals attraction and the hydration force repulsion. Therefore, it is not obvious that this addition should lead to any change in the swelling of the lamellae.

The experimental results show, however, that when dodecanol is added to the binary systems of AD - water and TAS - water, the uptake of water in the lamellar phase is increasing. An addition of about 10 % w/w dodecanol to the TAS - water system gives rise to a considerably stronger hydration force repulsion than was observed in the binary surfactant - water system. This effect is, however, not as drastic as if a charged component were added to the binary system.

The electrostatic continuum theory for the hydration force, suggested by Jönsson and Wennerström (3, 4), was previously successfully used to explain the effect of the polar head groups on the strength of the hydration force (2). The same theoretical model is also able to predict the increasing swelling of the lamellar phase when alcohol is added to the system.

In this model, both the water and the hydrocarbon layers are treated as continuous media, and the hydration force is due to the dielectric discontinuities at the water - hydrocarbon interfaces. A polar molecule fixed at a bilayer surface induces polarization charges at the interfaces. This interaction is in the model described in terms of the so called image charges. The important feature is that there are two contributions to the interactions. Replacing the water by hydrocarbon in the outer solvation region for the polar head groups gives rise to a repulsive image charge,

while the direct interaction between the head groups of opposing lamellae leads to an attractive interaction.

In the model, the polar layers are placed in the region with the lowest dielectric permittivity, a distance Δ from the dielectric discontinuity.

Therefore, even if the attractive image charge is larger than the repulsive one, it begins to operate further away from the opposing bilayer. At small separations, the net interaction between the bilayers is repulsive, but it becomes attractive at longer distances. The distance where the attractive contribution begins to dominate is strongly dependent on the value of Δ .

According to the theory, the osmotic pressure, Π , between the bilayers can be written by modifying slightly the eq. (16) in ref. (4):

$$\begin{aligned} \Pi \approx 1.3 * 10^{10} * \frac{32.5}{A_0} * \left\{ \frac{0.94}{(2 * L + \Delta)^4} - \frac{1.94}{(2 * L + 17.2 * \Delta)^4} * \right. \\ \left. * \left[1 + \frac{0.75 * A_0}{(2 * L * 65)} * \left(1 + \ln \left[\frac{0.75 * A_0}{65 * 2 * L * 4} \right] \right) \right] \right\} \quad (1) \end{aligned}$$

where $2 * L$ is the water layer thickness (Fig. 2) and A_0 is the area per charged head group in the lamellar aggregate.

It should be noticed that the eq. (1) is a linearized approximation of the exact equation (4), and thus only valid when $\sqrt{(2 * A_0 / \pi)} \ll 2 * L$. On the other hand, at high A_0 values when the equation can not be used, the lamellar aggregates would contain so much dodecanol that the lamellar phase structure would no longer be stable relative to other phases.

In the eq. (1), the first, positive term in the parentheses represents the repulsive image charge and the second, negative term the attractive correlation interaction. The effect of adding an uncharged amphiphile in the system is merely to dilute the charged head groups in the lamellar aggregate, i.e. to increase the value of A_0 . As can be seen from eq. (1), the repulsive term is only dependent of A_0 as $1/A_0$. This is because the repulsive contribution is due to the interaction between a charge and its own image charge which is not affected by the dilution. On the other hand, the attractive term has a stronger dependence on A_0 , because the number of interacting head groups of opposing lamellae is decreased by the dilution.

In Fig. 6, the osmotic pressure from eq. (1) is plotted as a function of A_0 for constant values of $2 * L = 11 \text{ \AA}$ and $\Delta = 0.1136 \text{ \AA}$, which are the values applicable for the TAS system. The diagram shows that when $A_0 < 25 \text{ \AA}^2$ the pressure is attractive, but above this value it becomes repulsive. The slope of the curve is first relatively steep, but the values of Π start to level off when A_0 reaches $50 \text{ \AA}^2$. As was mentioned before, higher values of A_0 than that are unrealistic.

The boundary between the lamellar phase and the two-phase region D + W in the TAS system can be approximately estimated in the following way. For the binary system TAS - water, the value of Δ is calculated from eq. (1) when $\Pi = 0$, $2 * L = 11 \text{ \AA}$ and $A_0 = 25 \text{ \AA}^2$.

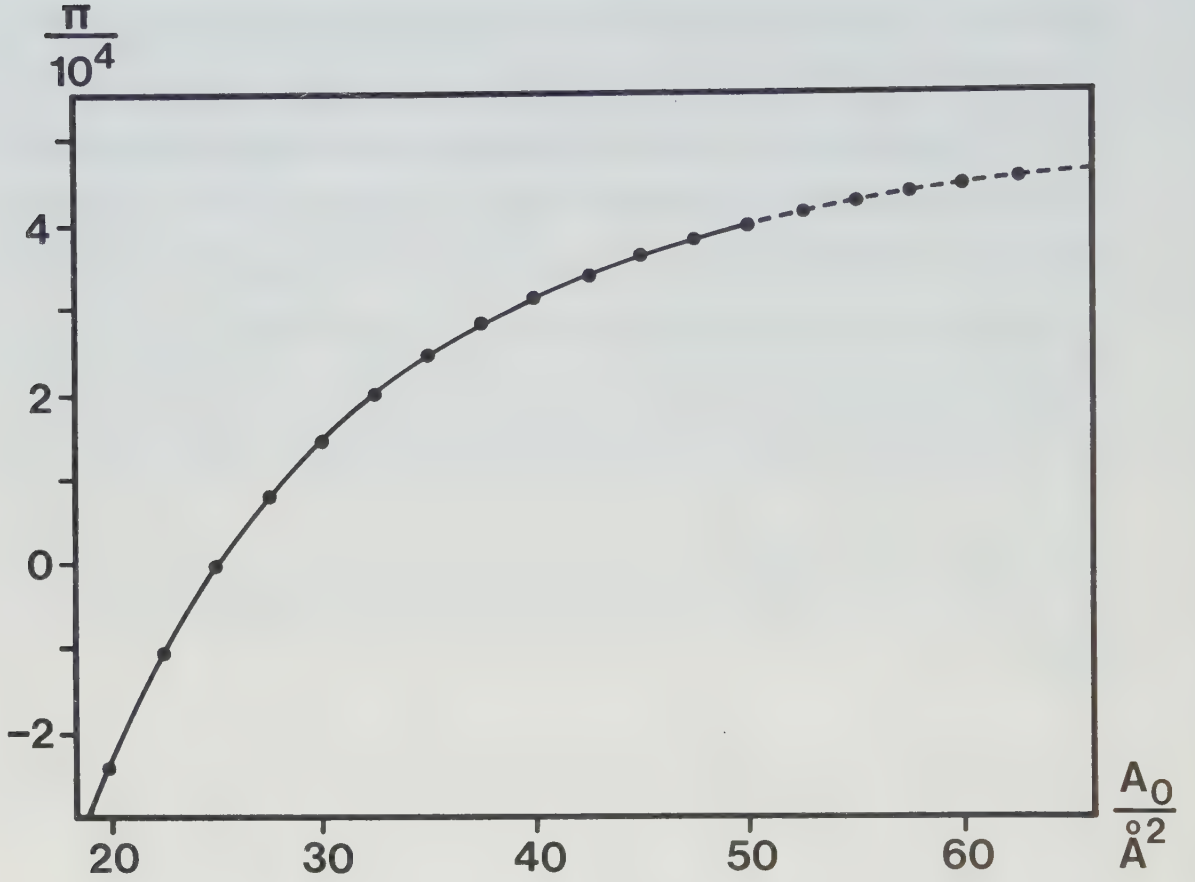


Fig. 6. A diagram showing the calculated values of the osmotic pressure between the lamellar bilayers, Π , as a function of the area per a charged group, A_0 , [from eq. (1)]. The thickness of the water layer is $2 * L = 11 \text{ \AA}$, and the value of $\Delta = 0.1136 \text{ \AA}$.

Solving the equation gives

$$\Delta \approx 0.1136 \text{ \AA}.$$

(2)

In further calculations, we assume that Δ has this constant value. The value of A_0 is then varied and the resulting $2 * L$ values are calculated from eq. (1) when $\Pi = 0$. From the molecular weights of the catanionic surfactant and dodecanol, the corresponding concentrations of the components in the ternary phase diagram TAS - dodecanol - water can easily be calculated for each value of A_0 and $2 * L$. The calculated phase boundary is shown in Fig. 7 .

The calculated phase boundary shows, indeed, increasing uptake of water in the lamellar phase when dodecanol is added to the system. However, the calculated phase boundary curves smoothly towards higher water contents without any abrupt change in the curvature at some specific dodecanol concentration, as was observed at 10 % w/w dodecanol in the experimental phase boundary.

It should be pointed out that the calculated phase boundary is quite a crude approximation. Firstly, in the eq. (1) we have assumed that the charge distribution is not effected by the decreased charge concentration, but this may not be true. If the equation were corrected in order to allow the charge distribution to change with dilution, this would lead to a stronger repulsive contribution. Secondly, the eq. (1) in itself is an approximation where only the first term of an infinite sum is taken into account. In order to correct this approximation, a small attractive contribution should be added to the eq. (1). This attractive term should, however, be much smaller than the repulsive term which is a result of the changes in the charge distribution.

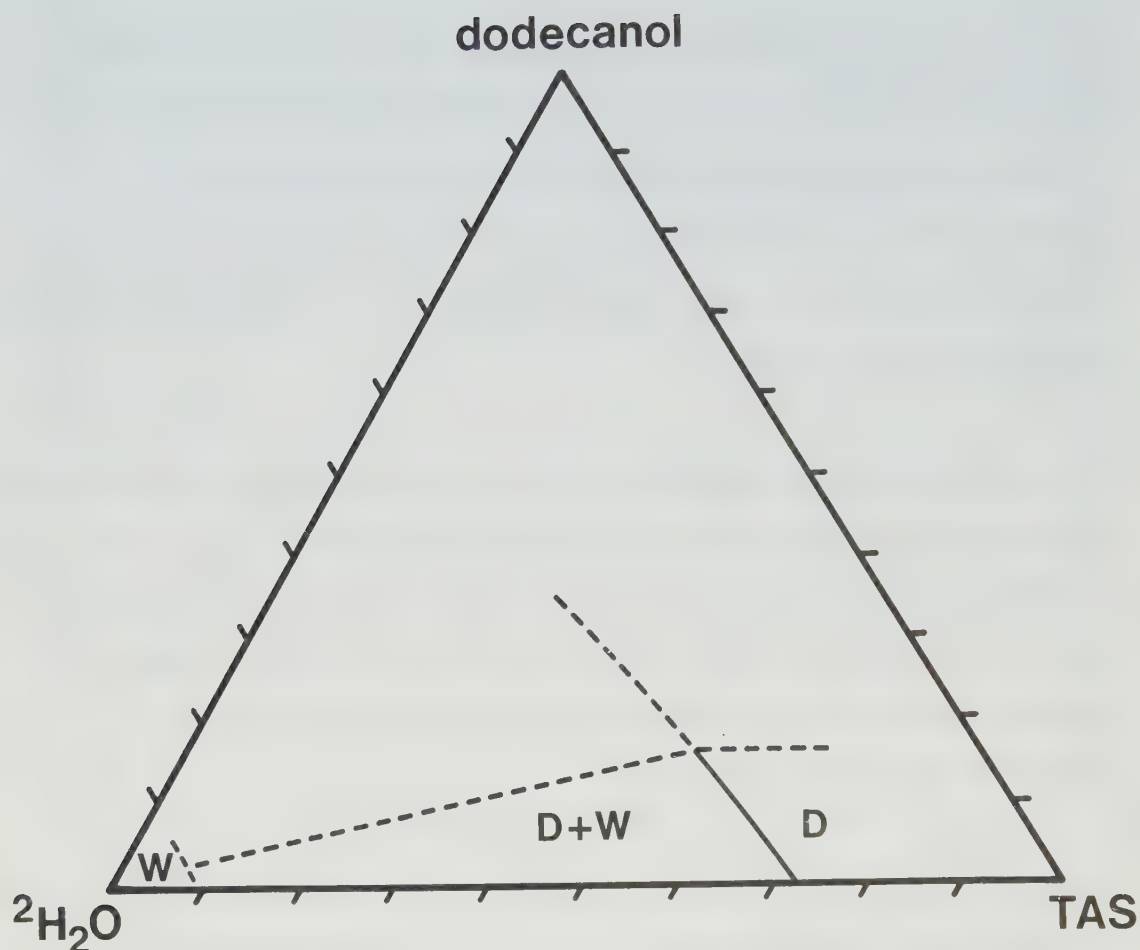


Fig. 7. A partial phase diagram showing the calculated boundary between the D-phase and the two-phase region D + W [from eq. (1), $\Pi = 0$ and $\Delta = 0.1136 \text{ \AA}$].

Furthermore, when $\Pi = 0$ is used as a condition that must be fulfilled for the phase equilibria, the van der Waals attraction is neglected. We assume

that when the bilayer separation is varied, the hydration force interaction changes much more rapidly than the van der Waals attraction (2, 4). Therefore, the curvature of the phase boundary is mainly determined by the hydration force interaction.

We can thus conclude that when the continuum theory is applied to the catanionic system, it can be shown that the addition of the uncharged amphiphile leads to an increasing swelling of the lamellar phase. The increase of the repulsive net force between the bilayers with increasing dodecanol concentration is mainly a result of the decrease in the attractive correlation force when the charge concentration in the lamellar aggregates is diluted by the addition of an uncharged component. On the contrary, the repulsive image charge contribution is much less dependent on the dilution of the charged headgroups.

TEMPERATURE DEPENDENT EFFECTS

Another interesting feature in the phase diagrams is that the extension of the lamellar phase towards the waterpoor region is effectively reduced by the existence of the crystalline phase.

In the TAS - dodecanol - water system, where the melting point of the crystals is relatively high, 428 K, the lamellar phase becomes more stable relative to the TAS crystals when the temperature is increased from the Krafft temperature 308 K to 333 K. On the contrary, the melting point of the AD crystals is only 345 K, and the addition of dodecanol to the

crystalline phase seems to have an effect to further lower the eutectic melting point of the AD crystals. Consequently, in the AD - dodecanol - water system it is the isotropic phase, with melted AD as the continuous medium, that becomes more stable relative to the lamellar phase with increasing temperature.

There are thus two main contributions to the fact that the stability of the lamellar phase in the AD system is strongly reduced compared to that of the lamellar phase in the TAS system, and that this trend seems to be even more striking with increasing temperature. The smaller polar head group of the AD surfactant leads to a weaker hydration force repulsion between the bilayers (2), so that the maximum uptake of water in the AD system is about 10 % w/w smaller than that in the TAS system. Above the temperature of the eutectic melting point of the crystalline AD phase, the stability of the lamellar phase is rapidly suppressed.

The effect of the same suppressing factors on the lamellar phase has also been observed in the theoretical study of the phase equilibria in a four component system catanionic surfactant - anionic surfactant - cationic surfactant - water (23). The thermodynamic model used in the calculations did not include a contribution from the hydration force repulsion and, furthermore, the chemical potential of the catanionic crystals was assumed to possess a constant, relatively low value compared with the chemical potential of the catanionic surfactant in the lamellar phase. Therefore, the calculated phase boundaries between the lamellar phase and the surfactant crystals gave that the lamellar phase was not stable in the binary system catanionic surfactant - water in that calculation.

SUMMARY

In this work, we have studied the phase equilibria in two ternary systems containing a catanionic surfactant, dodecanol and water.

The experimental phase diagrams show that adding an uncharged amphiphilic molecule to the binary catanionic surfactant - water systems gives rise to a stronger hydration force repulsion between the lamellar bilayers. This observation can be explained by the continuum theory which is suggested in order to describe the molecular origin of the hydration force. When the charge concentration in the lamellar aggregates is diluted by the addition of an uncharged amphiphile, the attractive component of the hydration force strongly decreases, while the repulsive component decreases only slightly.

As the dodecanol concentration in the lamellar phase reaches a value when the lamellar phase no longer is stable, the formation of reversed hexagonal phase and at still higher dodecanol concentrations the formation of a reversed micellar phase becomes favoured.

In one of the ternary systems (TAS - dodecanol - water), the melting point of the surfactant crystals is relatively high, so that the lamellar phase becomes more stable relative to the crystals with increasing temperature, in the temperature range 308 - 333 K. But in the other system (AD - dodecanol - water), the eutectic melting point of the surfactant crystals is lower and the melted surfactant forms an isotropic phase. In the same temperature range as above, an increasing temperature favours the extension of the isotropic phase in this system.

An interesting subject for the further studies is the effect of other types of components added to the binary catanionic surfactant - water systems. Furthermore, it is important to study different catanionic surfactants, in order to clarify if the phase behaviour in the studied systems represents a general pattern common to all catanionic systems. Work along this line is in progress in our laboratory.

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IV

Phase equilibria in systems containing both an anionic and a cationic amphiphile. A thermodynamic model calculation

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Abstract: We have studied the equilibrium between a lamellar phase and crystalline salts in a four-component system containing both a cationic and an anionic surfactant in water. The chemical potentials for the different components have been derived from a thermodynamic model for the free energy.

In our model system there are four salts that can precipitate: A^+X^- , A^-X^+ , A^+A^- and X^+X^- . A^+ and A^- are, respectively, a cationic and an anionic surfactant; X^- and X^+ are the corresponding counterions. The system is represented as a trigonal bipyramid. We have calculated the equilibrium between a lamellar phase and crystalline phases A^+A^- , A^-X^+ and A^+X^- with different weight fractions of A^+A^- .

The observed instability gap between the two lamellar regions around equal amounts of A^+X^- and A^-X^+ can be explained by the fact that dispersion attraction between the amphiphilic plates dominates over the electrostatic repulsion. The high entropy in the lamellar liquid crystal compared with a common crystal can be the reason for the extension of the lamellar stability region to very low water contents in the vicinity of the instability gap.

Key words: Phase equilibria, thermodynamic model, four-component systems

Introduction

Surfactant-water systems show a rich polymorphism and in addition to isotropic solutions and crystals a range of different liquid crystalline phases can form [1, 2]. The phase behaviour provides an essential clue to the understanding of the properties of surfactant systems and a large amount of experimental work has been devoted to determine phase equilibria. The theoretical description of the thermodynamic properties of the system has been studied to a much lesser extent.

In a series of papers we have developed a model for the thermodynamic properties of ionic surfactant-water systems [3–5]. This has led to fairly satisfactory description of phase equilibria in two and three component systems. As a continuation of this work we present a study of a model four-component system $H_2O - A^-X^+ - A^+X^-$ where A^- and A^+ are an anionic and a cationic surfactant, respectively, while X^+X^- forms an ordinary electrolyte. Dealing with four components in studies of phase equilibria poses a substantial problem due to the complexity

introduced by having at least three degrees of freedom within the one-phase areas. A model study is helpful in sorting out some of these difficulties.

The representation of the four-component system

A system produced by a solvent (water) and two simple salts A^+X^- and A^-X^+ with no common ion has four components in the sense used in connection with the Gibbs phase rule. There are four possible simple crystalline salts for the system since in addition to A^+X^- and A^-X^+ one can have A^+A^- and X^+X^- . In principle all four of these salts can form and to have a useful graphical representation of the system all of them should be represented as a point in the diagram. For given values of the intensive variables temperature and pressure the conventional triangular diagram for a three component system can be extended using a trigonal bipyramid as illustrated in figure 1. In this diagram there are three degrees of freedom and every possible composition can be represented.

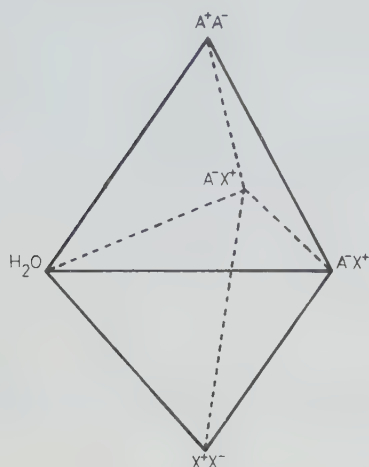


Fig. 1. A trigonal bipyramid representing the four-component system $H_2O - A^-X^+ - A^+X^- - A^+A^-$

The model system

We have chosen to study a model system containing an anionic surfactant A^-X^+ and a cationic surfactant A^+X^- where X^+ and X^- are assumed to be simple ions as Na^+ and Cl^- , respectively. Such a system could show interesting and unique properties, which should be sensitive to the ratio A^+/A^- . A particular feature is that the crystal A^+A^- is expected to be particularly stable. As a consequence we have concentrated on the possible equilibria with such a crystalline phase. For most soaps it is the lamellar phase that is the most stable liquid crystalline phase at higher concentrations and this is the other phase we consider. Thus the aim is to describe the equilibrium between crystalline phases A^+A^- , A^-X^+ and A^+X^- and a lamellar phase with varying ratio A^+/A^- . The simple salt X^+X^- is considered strongly water soluble. As a consequence of the restriction to one

liquid crystalline phase only a partial phase diagram is obtained. However, since our primary aim is to illustrate some general properties of a particular type of four-component system the restriction to few phases only provides a useful simplification.

The lamellar phase consists of aqueous layers with thickness, $2L$, alternating with surfactant bilayers, thickness $2b$, as illustrated in figure 2. The surfactant molecules are assumed to be totally incorporated into the lamella making the average charge density determined by the composition and the area per molecule. The ions X^+ and X^- are assumed to reside in the aqueous layer, where they partly have the role of counterions, X^+ or X^- depending on the A^+/A^- ratio, and partly the role of a screening electrolyte.

The thermodynamic model

Most parts of the thermodynamic model used have been presented previously, in [3–5]. We will therefore here only give a brief summary of the different energy contributions and their effect on the chemical potentials.

The free energy G of a lamellar system according to the model is written as

$$G = n_{H_2O} \mu_{H_2O}^0 + n_{A^-X^+} \mu_{A^-X^+}^0 + n_{A^+X^-} \mu_{A^+X^-}^0 + n_{A^-A^+} \mu_{A^-A^+}^0 + G_S + G_{el} - TS_{mix} + G_{DISP} \quad (1)$$

where μ_i^0 is the standard chemical potential of component i , G_S a surface free energy, G_{el} an electrostatic free energy, S_{mix} the entropy from the mixing of the components and G_{DISP} the free energy from the dispersion interactions.

G_S the surface free energy is assumed to follow the empirical equation [5]

$$G_S = \gamma_+ \cdot n_{A^+} \cdot A_+ + \gamma_- \cdot n_{A^-} \cdot A_- \quad (2)$$

where γ_+ and γ_- are experimentally determined constants, A_+ and A_- the surface area of the cationic respectively anionic amphiphile. The total area A between water and hydrocarbon parts may then be written as

$$A = n_{A^+} A_+ + n_{A^-} A_- \quad (3)$$

The contributions to the chemical potentials from the surface free energy will then be



Fig. 2. Schematic representation of a lamellar system. $2L$ is the thickness of water layer and $2b$ the thickness of surfactant bilayer

$$\mu_{A^+}^S = \gamma_+ A_+ \quad (4a)$$

$$\mu_{A^-}^S = \gamma_- A_- \quad (4b)$$

The contribution to the chemical potentials from the electrostatic free energy G_{el} and the entropy of mixing TS_{mix} are [3]

$$\mu_{H_2O}^{el-TS} = -N_A kT V_{H_2O} \cdot (c_+(0) + c_-(0)) \quad (5a)$$

$$\mu_{A^-X^+}^{el-TS} = kT \ln(c_+(L) \cdot X_-) - A_- \cdot 2E_{el}/A \quad (5b)$$

$$\mu_{A^+X^-}^{el-TS} = kT \ln(c_-(L) \cdot X_+) - A_+ \cdot 2E_{el}/A \quad (5c)$$

$$\mu_{X^+X^-}^{el-TS} = kT \ln(c_+(0) \cdot c_-(0)) \quad (5d)$$

for a lamellar system. Here V_{H_2O} is the volume of a water molecule, $c_i(0)$ and $c_i(L)$ are the concentrations of component i at $z = 0$ respectively $z = L$, (cf. fig. 2). X_i is the mole fraction in the amphiphilic aggregate of component i and E_{el} the energy of the ion-ion interaction. This is for a lamellar phase [4].

$$E_{el} = kT \cdot \{(n_{A^-X^+} + n_{A^+X^-} + 2 \cdot n_{X^+X^-}) - N_A \cdot L \cdot A \cdot (c_+(0) + c_-(0))\} \quad (6)$$

The dispersion energy G_{DISP} may for an infinite array of water and hydrocarbon sheets be written as [6]

$$G_{DISP}/A = -\frac{H}{48\pi b^2} \left\{ \frac{1}{2} + \sum_{j=1}^{\infty} \frac{y^4}{j^4} \cdot \frac{3 - (y^2/j^2)}{[1 - (y^2/j^2)]^2} \right\} = -f(y)/b^2 \quad (7)$$

where H is the Hamaker constant, $2b$ the thickness of a hydrocarbon sheet and y the volume fraction of hydrocarbon

$$y = \frac{b}{b+L} \quad (8)$$

The dispersion energy is in equation (7) assumed to be zero when $L \rightarrow \infty$ and $b \rightarrow \infty$. The contributions to the chemical potentials from the dispersion energy will then be

$$\mu_{H_2O}^{DISP} = \frac{V_{H_2O}}{b^3} \cdot y^2 \cdot f'(y) \quad (9a)$$

$$\mu_{A^-X^+}^{DISP} = -\frac{A_-}{b^2} (f(y) + (y - y^2) \cdot f'(y)) \quad (9b)$$

$$\mu_{A^+X^-}^{DISP} = -\frac{A_+}{b^2} (f(y) + (y - y^2) \cdot f'(y)) \quad (9c)$$

The chemical potentials may now be obtained by combining equations (1), (4), (5) and (9).

$$\mu_{H_2O} = \mu_{H_2O}^0 - N_A kT V_{H_2O} (c_+(0) + c_-(0)) + \frac{V_{H_2O}}{b^3} \cdot y^2 \cdot f'(y) \quad (10a)$$

$$\mu_{A^-X^+} = \mu_{A^-X^+}^0 + kT \ln(c_+(L) \cdot X_-) + A_- \cdot \{\gamma_- - 2E_{el}/A - (f(y) + (y - y^2)f'(y)/b^2)\} \quad (10b)$$

$$\mu_{A^+X^-} = \mu_{A^+X^-}^0 + kT \ln(c_-(L) \cdot X_+) + A_+ \cdot \{\gamma_+ - 2E_{el}/A - (f(y) + (y - y^2)f'(y)/b^2)\} \quad (10c)$$

$$\mu_{X^+X^-} = \mu_{X^+X^-}^0 + kT \ln(c_+(0) \cdot c_-(0)) \quad (10d)$$

$$\mu_{A+A-} = \mu_{A^+X^-} + \mu_{A^-X^+} - \mu_{X^+X^-} \quad (10e)$$

In applying the equations for the chemical potentials one must know the areas A_+ and A_- of the amphiphilic molecules as well as the thickness of the hydrocarbon sheet $2b$. These quantities may for systems with low charge densities be calculated from the volume V_i and the maximum length $b_{i \max}$ of the amphiphile molecules.

$$A_i = V_i/b_{i \max} \quad (11)$$

The thickness of the hydrocarbon sheet will then be

$$2b = 2 \cdot \frac{n_{A^+} \cdot V_{A^+} + n_{A^-} \cdot V_{A^-}}{n_{A^+} \cdot A_{A^+} + n_{A^-} \cdot A_{A^-}} \quad (12)$$

This procedure may however not be used for systems with high charge densities since equation (11) is then no longer valid (see reference 4). The condition for optimal size

$$\left(\frac{\partial G}{\partial b} \right)_{n_j} = 0 \quad (13)$$

must instead be used to determine A_i and b . The partial derivative $(\partial G/\partial b)_{n_j}$ is

$$\left(\frac{\partial G}{\partial b} \right)_{n_j} = -A \cdot \{\gamma - 2E_{el}/A - 3 \cdot f(y)/b^2\}/b \quad (14)$$

following Appendix 2 of reference 4.

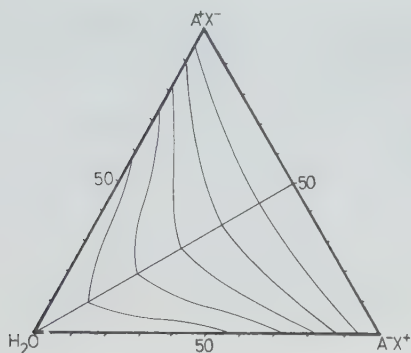


Fig. 3. The chemical potential of water remains unchanged along the curves drawn in the phase diagram

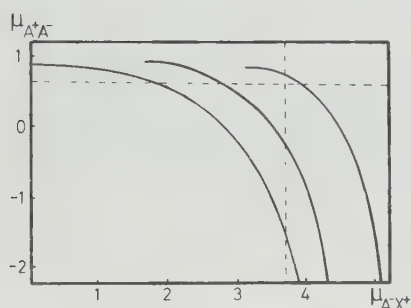


Fig. 4. The full lines represent the chemical potential of A^+A^- ($\mu_{A^+A^-}$) as a function of the chemical potential of A^-X^+ ($\mu_{A^-X^+}$) for three different L -values. The dotted lines show the constant chemical potentials of the crystalline salts

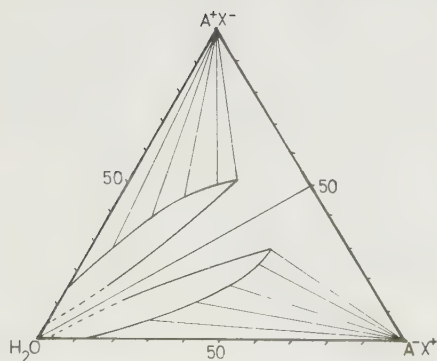


Fig. 5. Tie-lines between a lamellar phase and the crystalline phase A^+X^- and A^-X^+

The computational procedure

For two or more phases in equilibrium the chemical potentials of all components should be equal in the two phases. Since the expressions for the chemical potentials in equations (10a–e) are fairly complex it poses a considerable computational problem to solve for the phase boundaries. At the present stage we are only considering one liquid crystalline phase, which introduces a significant simplification of the calculations. For the crystalline phases fixed values are given for the crystallized component and for the other components the chemical potentials vary very strongly with minute additions of the particular component. Consequently one can satisfy the equilibrium with the liquid crystal for any values of the chemical potential of the impurity. It is assumed that mixed crystals do not form.

For the lamellar phase equations (10a–e) apply. This phase can in the model be in equilibrium with either of the three crystals A^+X^- , A^-X^+ and A^-A^+ . To find these equilibria a stepwise procedure is used.

i) Confine the composition in the lamellar phase to a particular plane $H_2O-A^-X^+-A^+X^-$ in the bipyramid.

ii) Choose a value for the water chemical potential.

iii) Choose a value for the thickness, $2L$, of the aqueous layer.

iv) Choose a value for $\alpha = c_+(0)/c_-(0)$. Using equation (10a) and the values assigned in ii)–iv) $c_+(0)$ and $c_-(0)$ are calculated.

v) Choose a value for the thickness, $2b$, of the surfactant bilayer.

vi) Solve the PB equation (see reference 7) and check that the value assigned to b is consistent with equations (12) and (14). If not go back to iv).

vii) Determine the composition from the solution of the PB equation. If it is not consistent with the particular plane in the bipyramid chosen in i) go back to v).

viii) Calculate $\mu_{A^-A^+}$ and $\mu_{A^-X^+}$. Go back to iii).

ix) When $\mu_{A^-A^+}$ and $\mu_{A^-X^+}$ have been calculated for a number of different L -values they are plotted in a diagram as shown in figure 3 and figure 4.

x) The chemical potentials of the crystalline salts are assigned particular values. They represent straight lines in figure 4. Equilibrium between a crystalline phase and the lamellar phase is obtained at the intersections in the plot.

xi) The composition in the lamellar phase for the two intersection points is calculated and one obtains one tie-line to a crystalline phase as illustrated for A^-X^+ and A^+X^- crystals in figure 5.

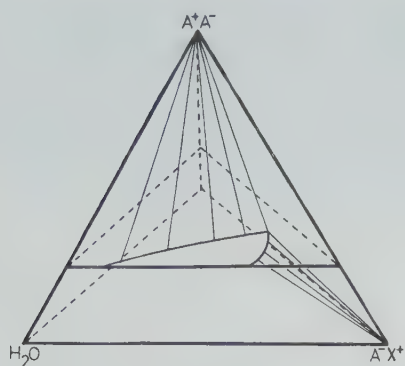


Fig. 6. The extension of the lamellar phase for a particular plane of the bipyramid and the tie-lines between the lamellar phase and the crystalline phases A^-X^+ and A^+A^- .

xii) The procedure is now repeated for a new choice of the water chemical potential.

xiii) The full phase diagram is obtained by choosing a new plane in the bipyramid.

Results

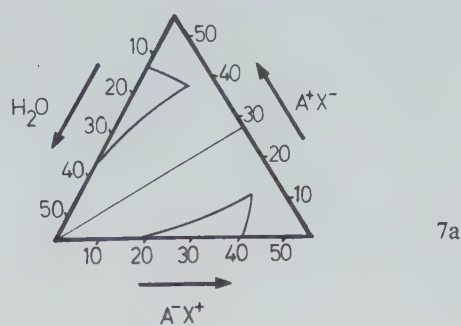
Calculations were performed for compositions in the upper part of the bipyramid since this is the region where equilibria with A^+X^- , A^-X^+ and A^+A^- crystals are of most interest. There is furthermore complete symmetry with respect to charge inversion in the model so it is sufficient to consider only one half of the bipyramid.

Figure 6 shows for a particular plane of the bipyramid the extension of the lamellar phase and also the tie-lines. Figures 7a–d show the extension of the lamellar phase for a series of planes.

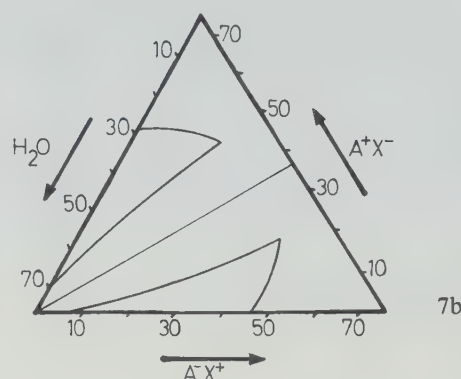
Discussion

The problems of applying the previously developed thermodynamic model to a four-component system has been investigated. It is shown that at least for the restricted applications to equilibria between a lamellar phase and crystals the computational problems can be solved using only a minicomputer. We further expect that the calculations will be of considerable help in the experimental studies of anionic surfactant-cationic surfactant-water systems that are currently performed in this laboratory.

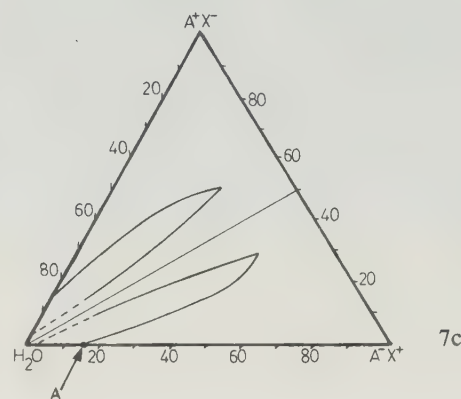
Due to the conceptual simplicity of the model it is fairly straightforward to interpret the resulting phase



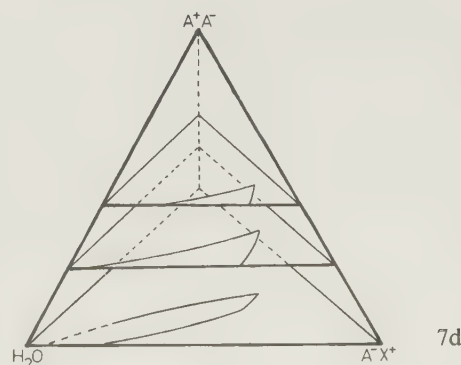
7a



7b



7c



7d

Fig. 7. The extension of the lamellar phase for a series of different weight fractions of A^+A^- . a) 45% w/w, b) 25% w/w and c) 0% w/w. d) The three planes of a)–c) represented in the bipyramid

equilibria qualitatively. For the pure binary system $\text{H}_2\text{O}-A^-X^+$ the lamellar phase is stable relative to the crystalline salt up to a certain concentration. This concentration is determined by the relative stability of the surfactant molecule in a liquid crystalline environment and in the crystal, i.e. the difference $\mu_{A^-X^+}^0(\text{crystal}) - \mu_{A^-X^+}^0(\text{liquid})$. In addition there is an effect of the electrostatics so that the more concentrated the system the higher is the chemical potential of the surfactant in the lamellar system. Thus the crystal will ultimately be the most stable as the concentration is increased. This determines the location of the point A in figure 7c. For the phase equilibria in the base plane of the bipyramid (fig. 7c) the addition of A^+X^- to the $\text{H}_2\text{O}-A^-X^+$ system has two effects. Since A^+ is incorporated into the lamella the surface charge density decreases, making the electrostatic interactions less important. Secondly there is an entropy of mixing term for the amphiphiles also decreasing their chemical potential. Thus the lamellar phase becomes more stable relative to the A^-X^+ crystals. The addition of A^+X^- leads on the other hand to an increase in the chemical potential of A^+A^- . The stability relative to the A^+A^- crystals is thus decreased. Eventually this leads to a precipitation of these crystals giving a new border line for the lamellar phase region. The point where the two precipitation limits meet lies on one of the edges of a three-phase region in the bipyramid. In this three-phase region with A^-X^+ and A^+A^- crystals in equilibrium with the lamellar phase there is still one degree of freedom

left. For an arbitrary point P in this three-phase region the composition in the lamellar phase is obtained by constructing the plane through P and the two corners A^+A^- and A^-X^+ . This plane intersects the edge of the lamellar phase region and this intersection gives the composition of the equilibrium lamellar phase at the composition P .

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